

PATENT COOPERATION TREATY

From the INTERNATIONAL BUREAU

PCT

NOTIFICATION OF ELECTION
(PCT Rule 61.2)Date of mailing (day/month/year)
17 July 2000 (17.07.00)To:

Assistant Commissioner for Patents
United States Patent and Trademark
Office
Box PCT
Washington, D.C.20231
ETATS-UNIS D'AMERIQUE

in its capacity as elected Office

International application No.
PCT/GB99/04209Applicant's or agent's file reference
SMC 60331/WOInternational filing date (day/month/year)
13 December 1999 (13.12.99)Priority date (day/month/year)
21 December 1998 (21.12.98)

Applicant

JAMES, Mark, Robert et al

1. The designated Office is hereby notified of its election made:

in the demand filed with the International Preliminary Examining Authority on:

20 June 2000 (20.06.00)

in a notice effecting later election filed with the International Bureau on:

2. The election was

was not

made before the expiration of 19 months from the priority date or, where Rule 32 applies, within the time limit under Rule 32.2(b).

The International Bureau of WIPO
34, chemin des Colombettes
1211 Geneva 20, Switzerland

Faxsimile No.: (41-22) 740.14.35

Authorized officer

Olivia RANAIVOJAONA

Telephone No.: (41-22) 338.83.38

INTERNATIONAL SEARCH REPORT

International Application No
PCT/GB 99/04209

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C09D11/00 C09B69/10

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 C09B C09D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 4 375 357 A (WINGARD JR ROBERT E ET AL) 1 March 1983 (1983-03-01) column 9 column 14 ---	1-19
X	FR 1 523 820 A (DAINICHISEIKA COLOR & CHEMICALS) 18 September 1968 (1968-09-18) page 2, column 1, paragraph 4 -page 3, column 1, paragraph 1 page 4, column 1, last paragraph page 12, column 2, last paragraph ---	1-19
X	EP 0 535 490 A (BASF AG) 7 April 1993 (1993-04-07) claim 1 ---	1-19 -/-



Further documents are listed in the continuation of box C.



Patent family members are listed in annex.

° Special categories of cited documents :

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier document but published on or after the international filing date
- "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"g" document member of the same patent family

Date of the actual completion of the international search

12 April 2000

Date of mailing of the international search report

25/04/2000

Name and mailing address of the ISA
European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl.
Fax: (+31-70) 340-3016

Authorized officer

Andriollo, G

INTERNATIONAL SEARCH REPORT

International Application No
PCT/GB 99/04209

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 048 214 A (CIBA GEIGY AG) 24 March 1982 (1982-03-24) page 13 ---	1-19
X	FR 2 107 876 A (RANK XEROX LTD) 12 May 1972 (1972-05-12) page 5, paragraph 2 ---	1-9
X	US 4 141 890 A (HEGAR GERT ET AL) 27 February 1979 (1979-02-27) claim 1 -----	1

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/GB 99/04209

Patent document cited in search report		Publication date	Patent family member(s)		Publication date
US 4375357	A	01-03-1983	NONE		
FR 1523820	A	18-09-1968	BE	698813 A	22-11-1967
			JP	48032586 B	06-10-1973
			NL	6706274 A	27-11-1967
EP 0535490	A	07-04-1993	DE	4132685 A	08-04-1993
			DE	59208569 D	10-07-1997
			JP	5239374 A	17-09-1993
			US	5434231 A	18-07-1995
			US	RE35407 E	17-12-1996
			US	5461131 A	24-10-1995
			US	5264507 A	23-11-1993
EP 0048214	A	24-03-1982	JP	57053510 A	30-03-1982
FR 2107876	A	12-05-1972	BE	772857 A	21-03-1972
			CA	959695 A	24-12-1974
			DE	2147158 A	20-04-1972
			GB	1377067 A	11-12-1974
			NL	7112852 A	24-03-1972
US 4141890	A	27-02-1979	CH	606304 A	31-10-1978
			BE	805656 A	04-04-1974
			CS	177866 B	31-08-1977
			DE	2349752 A	11-04-1974
			FR	2202089 A	03-05-1974
			GB	1449251 A	15-09-1976
			IT	996243 B	10-12-1975
			JP	49073430 A	16-07-1974

PATENT COOPERATION TREATY

PCT

INTERNATIONAL SEARCH REPORT

(PCT Article 18 and Rules 43 and 44)

Applicant's or agent's file reference SMC 60331/WO	FOR FURTHER ACTION see Notification of Transmittal of International Search Report (Form PCT/ISA/220) as well as, where applicable, item 5 below.	
International application No. PCT/GB 99/ 04209	International filing date (day/month/year) 13/12/1999	(Earliest) Priority Date (day/month/year) 21/12/1998
Applicant AVECIA LIMITED et al.		

This International Search Report has been prepared by this International Searching Authority and is transmitted to the applicant according to Article 18. A copy is being transmitted to the International Bureau.

This International Search Report consists of a total of 3 sheets.
 It is also accompanied by a copy of each prior art document cited in this report.

1. Basis of the report

- a. With regard to the language, the international search was carried out on the basis of the international application in the language in which it was filed, unless otherwise indicated under this item.
 - the international search was carried out on the basis of a translation of the international application furnished to this Authority (Rule 23.1(b)).
- b. With regard to any nucleotide and/or amino acid sequence disclosed in the international application, the international search was carried out on the basis of the sequence listing :
 - contained in the international application in written form.
 - filed together with the international application in computer readable form.
 - furnished subsequently to this Authority in written form.
 - furnished subsequently to this Authority in computer readable form.
 - the statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.
 - the statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished

2. Certain claims were found unsearchable (See Box I).3. Unity of Invention is lacking (see Box II).

4. With regard to the title,

- the text is approved as submitted by the applicant.
- the text has been established by this Authority to read as follows:

5. With regard to the abstract,

- the text is approved as submitted by the applicant.
- the text has been established, according to Rule 38.2(b), by this Authority as it appears in Box III. The applicant may, within one month from the date of mailing of this international search report, submit comments to this Authority.

6. The figure of the drawings to be published with the abstract is Figure No.

- as suggested by the applicant.
- because the applicant failed to suggest a figure.
- because this figure better characterizes the invention.

None of the figures.

INTERNATIONAL SEARCH REPORT

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Further documents are listed in the continuation of box C.

Patent family members are listed in annex.

° Special categories of cited documents :

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"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search

Date of mailing of the international search report

12 April 2000

25/04/2000

Name and mailing address of the ISA
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NL - 2280 HV Rijswijk
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Fax: (+31-70) 340-3016

Authorized officer

Andriollo, G

INTERNATIONAL SEARCH REPORT

International Application No
PCT/GB 99/04209

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

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International Application No

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			NL 6706274 A		27-11-1967
EP 0535490	A	07-04-1993	DE 4132685 A		08-04-1993
			DE 59208569 D		10-07-1997
			JP 5239374 A		17-09-1993
			US 5434231 A		18-07-1995
			US RE35407 E		17-12-1996
			US 5461131 A		24-10-1995
			US 5264507 A		23-11-1993
EP 0048214	A	24-03-1982	JP 57053510 A		30-03-1982
FR 2107876	A	12-05-1972	BE 772857 A		21-03-1972
			CA 959695 A		24-12-1974
			DE 2147158 A		20-04-1972
			GB 1377067 A		11-12-1974
			NL 7112852 A		24-03-1972
US 4141890	A	27-02-1979	CH 606304 A		31-10-1978
			BE 805656 A		04-04-1974
			CS 177866 B		31-08-1977
			DE 2349752 A		11-04-1974
			FR 2202089 A		03-05-1974
			GB 1449251 A		15-09-1976
			IT 996243 B		10-12-1975
			JP 49073430 A		16-07-1974

PATENT COOPERATION TREATY

PCT

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

(PCT Article 36 and Rule 70)

Applicant's or agent's file reference SMC 60331/WO	FOR FURTHER ACTION	See Notification of Transmittal of International Preliminary Examination Report (Form PCT/IPEA/416)
International application No. PCT/GB99/04209	International filing date (day/month/year) 13/12/1999	Priority date (day/month/year) 21/12/1998
International Patent Classification (IPC) or national classification and IPC C09D11/00		
Applicant AVECIA LIMITED et al.		
<p>1. This international preliminary examination report has been prepared by this International Preliminary Examining Authority and is transmitted to the applicant according to Article 36.</p> <p>2. This REPORT consists of a total of 4 sheets, including this cover sheet.</p> <p><input checked="" type="checkbox"/> This report is also accompanied by ANNEXES, i.e. sheets of the description, claims and/or drawings which have been amended and are the basis for this report and/or sheets containing rectifications made before this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions under the PCT).</p> <p>These annexes consist of a total of 4 sheets.</p>		
<p>3. This report contains indications relating to the following items:</p> <ul style="list-style-type: none"> I <input checked="" type="checkbox"/> Basis of the report II <input type="checkbox"/> Priority III <input type="checkbox"/> Non-establishment of opinion with regard to novelty, inventive step and industrial applicability IV <input type="checkbox"/> Lack of unity of invention V <input checked="" type="checkbox"/> Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement VI <input type="checkbox"/> Certain documents cited VII <input type="checkbox"/> Certain defects in the international application VIII <input type="checkbox"/> Certain observations on the international application 		

Date of submission of the demand 20/06/2000	Date of completion of this report 10.04.2001
Name and mailing address of the international preliminary examining authority:  European Patent Office D-80298 Munich Tel. +49 89 2399 - 0 Tx: 523656 epmu d Fax: +49 89 2399 - 4465	Authorized officer Andriollo, G Telephone No. +49 89 2399 8301



**INTERNATIONAL PRELIMINARY
EXAMINATION REPORT**

International application No. PCT/GB99/04209

I. Basis of the report

1. With regard to the **elements** of the international application (*Replacement sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to this report since they do not contain amendments (Rules 70.16 and 70.17)*):

Description, pages:

1-7,9-11,13-26	as originally filed		
8,12	as received on	05/12/2000 with letter of	01/12/2000

Claims, No.:

17-19	as originally filed		
1-16	as received on	05/12/2000 with letter of	01/12/2000

2. With regard to the **language**, all the elements marked above were available or furnished to this Authority in the language in which the international application was filed, unless otherwise indicated under this item.

These elements were available or furnished to this Authority in the following language: , which is:

- the language of a translation furnished for the purposes of the international search (under Rule 23.1(b)).
- the language of publication of the international application (under Rule 48.3(b)).
- the language of a translation furnished for the purposes of international preliminary examination (under Rule 55.2 and/or 55.3).

3. With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, the international preliminary examination was carried out on the basis of the sequence listing:

- contained in the international application in written form.
- filed together with the international application in computer readable form.
- furnished subsequently to this Authority in written form.
- furnished subsequently to this Authority in computer readable form.
- The statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.
- The statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished.

4. The amendments have resulted in the cancellation of:

- the description, pages:
- the claims, Nos.:
- the drawings, sheets:

**INTERNATIONAL PRELIMINARY
EXAMINATION REPORT**

International application No. PCT/GB99/04209

5. This report has been established as if (some of) the amendments had not been made, since they have been considered to go beyond the disclosure as filed (Rule 70.2(c)):

(Any replacement sheet containing such amendments must be referred to under item 1 and annexed to this report.)

6. Additional observations, if necessary:

**V. Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability;
citations and explanations supporting such statement**

1. Statement

Novelty (N)	Yes:	Claims
	No:	Claims 1-16
Inventive step (IS)	Yes:	Claims
	No:	Claims 1-16
Industrial applicability (IA)	Yes:	Claims 1-16
	No:	Claims

2. Citations and explanations
see separate sheet

**INTERNATIONAL PRELIMINARY
EXAMINATION REPORT - SEPARATE SHEET**

International application No. PCT/GB99/04209

V

1. The following document is cited in the search report; the numbering will be adhered to in the rest of the procedure :
D1 : US-A-4375357.
2. The present application does not satisfy the criterion set forth in Article 33(2) PCT because the subject-matter of claims 1-16 lacks novelty in view of D1. D1 relates to aqueous inks. The dye is attached to the polymer through several possible groups. Several embodiments consist of a covalent -O- bond (see embodiments 24 and 32 at col. 9 and 14 respectively). The molecular weights can vary between 1.000 and 2.000.000 (average values). The preferred values are between 5.000 and 500.000 (see col. 15, l. 46-52). Since the molecular weights fall within the range of present claim 1, the viscosity will logically follow the same trend. Furthermore, an azo group can be introduced via a diazotisation reaction (see col. 16, lines 4-42). On the other hand, claim 2 is a "product-by-process claim" and, therefore, it is allowable only if the product as such fulfils the requirements for patentability, i. e. if it is new and inventive. The fact that the claimed product has been formed by a certain process does not automatically render said product novel in view of the product prepared by another way.

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PCT/GB99/04209

In one embodiment the olefinic water-dissipatable polymer may be prepared by polymerising an acrylic oligomer having water-dispersing groups and at least one olefinically unsaturated terminal group in the presence of one or more olefinically unsaturated monomers having a hydroxy functional group or a group which is convertible to a hydroxy functional group, and optionally one or more olefinically unsaturated monomers which are free from water-dispersing groups and/or one or more olefinically unsaturated monomers having water-dispersing groups.

Alternatively an acrylic oligomer with at least one olefinically unsaturated terminal group and which is free from water-dispersing groups may be polymerised in the presence of one or more olefinically unsaturated monomers having a hydroxy functional group or a group which is convertible to a hydroxy functional group and one or more olefinically unsaturated monomers having water-dispersing groups.

Preferred polymerisation methods include solution polymerisation, emulsion polymerisation, suspension polymerisation and solution/dispersion polymerisation and such general methods as are well known in the art. More preferably aqueous or non-aqueous solution polymerisation and emulsion polymerisation is used and most preferably solution polymerisation is used.

If desired, an initiator may be used to assist the water-dissipatable olefinic polymer formation. Suitable initiators are free-radical generators. Examples of catalysts include azobis compounds, peroxides, hydroperoxides, redox catalysts, etc., for example, potassium persulfate, ammonium persulfate, tert-butyl peroctoate, benzoyl peroxide, isopropyl percarbonate, 2,4-dichlorobenzoyl peroxide, methyl ethyl ketone peroxide, cumene hydroperoxide, dicumyl peroxide, azobisisobutyronitrile, azobis(2-amidino-propane)hydrochloride and the like.

Typically 0.05 to 5% by weight of initiator is used relative to the total weight of the monomers. Preferably the polymerisation is performed in the presence of an emulsifying agent.

The molecular weight of the olefinic water-dissipatable polymer may be controlled by the addition of chain transfer agents and/or through the adjustment of the ratio of the concentration of monomers relative to the concentration of initiator during the course of the polymerisation. Typical chain transfer agents are thiols, halocarbons and cobalt macrocycles.

When the water-dissipatable polymer is a polyester or polyurethane it may be prepared by conventional techniques, for example as described in PCT/GB99/00656 (polyurethanes) or PCT/GB98/01683 (polyesters) using a monomer carrying a protected hydroxy functional group to form the water-dissipatable polymer followed by removal of the protecting group prior to reaction with a colorant, a colorant precursor, or a bridging compound to give a covalent -O-link.

When the water-dissipatable polymer is prepared by the polymerisation of

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The ink preferably has a pH from 3 to 11, more preferably from 4 to 10. The pH selected will depend to some extent on the desired cation for colorant and the materials used to construct the ink jet printer head. The desired pH may be obtained by the addition of an acid, base or a pH buffer. Where a base is used this is preferably the same base as was used to neutralise any anionic dispersing group during the preparation of the water-dissipatable polymer of the invention.

mPa.s (cP)

mPa.s (cP)

The viscosity of the ink is preferably less than 20 μ N.s, more preferably less than 15 μ N.s, especially less than 10 μ N.s at 20°C.

Preferably the ink has been filtered through a filter having a mean pore size below 10 μ m, preferably below 5 μ m, more preferably below 2 μ m, especially below 0.45 μ m. In this way particulate matter is removed which could otherwise block fine nozzles in an ink jet printer.

Preferably the ink contains less than 500 ppm, more preferably less than 250 ppm, especially less than 100 ppm of in total of divalent and trivalent metal ions.

The inks of the present invention have the advantage that they are suitable not only for the use in piezoelectric ink jet printers but also in thermal and continuous ink jet printers. Many other inks based on polymers work poorly or even not at all in thermal ink jet printers.

Inks of the present invention form discrete droplets on the substrate with little tendency for diffusing. Consequently sharp images with excellent print quality and little if any bleed between colours printed side by side can be obtained. Furthermore the inks show good storage stability, wet and light fastness and fastness to both acidic and alkaline highlighter pens.

A third aspect of the invention provides a process for printing an image on a substrate comprising applying thereto an ink according to the second aspect of the present invention by means of an ink jet printer.

The ink jet printer preferably applies the ink to the substrate in the form of droplets which are ejected through a small nozzle onto the substrate. Preferred ink jet printers are piezoelectric ink jet printers and thermal ink jet printers. In thermal ink jet printers, programmed pulses of heat are applied to the ink in a reservoir by means of a resistor adjacent to the nozzle, thereby causing the ink to be ejected in the form of small droplets directed towards the substrate during relative movement between the substrate and the nozzle. In piezoelectric ink jet printers the oscillation of a small crystal causes ejection of the ink from the nozzle.

The substrate is preferably a paper, plastic, or textile material, more preferably a paper, an overhead projector slide or a textile material, especially paper.

Preferred papers are plain, coated or treated papers which may have an acid, alkaline or neutral character. Most preferably the substrate is a coated paper.

According to a fourth feature of the invention there is provided an ink jet printer cartridge, optionally refillable, containing an ink as hereinbefore defined.

AMENDED CLAIMS

1. An ink having a viscosity less than 20 mPa.s (cP) at 20°C, comprising the components:
 - 5 (a) a water-dissipatable polymer having colorant attached thereto through a covalent -O- link, wherein the water-dissipatable polymer has a Mn less than 25,000; and
 - (b) a liquid medium.
- 10 2. An ink according to claim 1 wherein the water-dissipatable polymer is obtainable by the reaction of a water-dissipatable polymer with pendant hydroxy functional groups with a colorant having a functional group capable of reacting with hydroxy functional groups.
- 15 3. An ink according to claim 1 wherein the colorant is attached to the water-dissipatable polymer by means of a reaction between a hydroxy group on the polymer with a colorant precursor thereby forming a covalent bond therebetween and subsequently converting the colorant precursor to a colorant.
- 20 4. An ink according to claim 1 wherein the colorant is attached to the water-dissipatable polymer by means of a reaction between a hydroxy group on the polymer with a bridging compound thereby forming a covalent bond therebetween and subsequently reacting the bridging compound with a colorant or colorant precursor.
- 25 5. An ink according to claim 4 wherein the colorant precursor is converted to a colorant by a process comprising a diazotisation reaction.
6. An ink according to claim 5 wherein the diazotisation reaction comprises the steps:
 - 30 (i) diazotising an amino group in the colorant precursor using a diazotising agent; and
 - (ii) coupling the product of step (i) with a coupling component forming an azo group therebetween.
- 35 7. An ink according to anyone of the preceding claims wherein the water-dissipatable polymer is an olefinic polymer.
8. An ink according to claim 7 wherein the olefinic polymer is obtainable from the polymerisation of one or more olefinically unsaturated monomers having water-dispersing groups, and one or more olefinically unsaturated monomers having hydroxy functional groups optionally in the presence of one or more olefinically unsaturated monomers which are free from water-dispersing and hydroxy functional groups.



9. An ink according to any one of the preceding claims wherein component (a) is completely dissipated in component (b).

5 10. An ink according to any one of the preceding claims which comprises from 0.5 to 50 parts of component (a) and from 50 to 99.5 parts of component (b), wherein all parts are by weight and the number of parts of (a) + (b) = 100.

10 11. An ink according to any one of the preceding claims wherein component (b) comprises water and an organic solvent.

12. An ink according to claim 11 where component (b) comprises from 40 to 95 parts of water and from 2 to 60 parts of water-miscible organic solvent.

15 13. An ink according to any one of the preceding claims for use in an ink jet printer.

14. A process for forming an image on a substrate comprising applying thereto an ink using an ink jet printer, characterised in that the ink is as defined in any one of the preceding claims.

20 15. A paper or an overhead projector slide printed with an ink as defined in any one of the preceding claims.

25 16. An ink jet printer cartridge, optionally refillable, containing an ink as defined in any one of the preceding claims.

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PATENT COOPERATION TREATY

PCT

RECD 12 APR 2001
14

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

(PCT Article 36 and Rule 70)

Applicant's or agent's file reference SMC 60331/WO	FOR FURTHER ACTION	See Notification of Transmittal of International Preliminary Examination Report (Form PCT/IPEA/416)
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This report is also accompanied by ANNEXES, i.e. sheets of the description, claims and/or drawings which have been amended and are the basis for this report and/or sheets containing rectifications made before this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions under the PCT).

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3. This report contains indications relating to the following items:

- I Basis of the report
- II Priority
- III Non-establishment of opinion with regard to novelty, inventive step and industrial applicability
- IV Lack of unity of invention
- V Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement
- VI Certain documents cited
- VII Certain defects in the international application
- VIII Certain observations on the international application

Date of submission of the demand 20/06/2000	Date of completion of this report 10.04.2001
Name and mailing address of the international preliminary examining authority:  European Patent Office D-80298 Munich Tel. +49 89 2399 - 0 Tx: 523656 epmu d Fax: +49 89 2399 - 4465	Authorized officer Andriollo, G Telephone No. +49 89 2399 8301



**INTERNATIONAL PRELIMINARY
EXAMINATION REPORT**

International application No. PCT/GB99/04209

I. Basis of the report

1. With regard to the elements of the international application (*Replacement sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to this report since they do not contain amendments (Rules 70.16 and 70.17)*):

Description, pages:

1-7,9-11,13-26 as originally filed

8,12 as received on 05/12/2000 with letter of 01/12/2000

Claims, No.:

17-19 as originally filed

1-16 as received on 05/12/2000 with letter of 01/12/2000

2. With regard to the **language**, all the elements marked above were available or furnished to this Authority in the language in which the international application was filed, unless otherwise indicated under this item.

These elements were available or furnished to this Authority in the following language: , which is:

- the language of a translation furnished for the purposes of the international search (under Rule 23.1(b)).
- the language of publication of the international application (under Rule 48.3(b)).
- the language of a translation furnished for the purposes of international preliminary examination (under Rule 55.2 and/or 55.3).

3. With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, the international preliminary examination was carried out on the basis of the sequence listing:

- contained in the international application in written form.
- filed together with the international application in computer readable form.
- furnished subsequently to this Authority in written form.
- furnished subsequently to this Authority in computer readable form.
- The statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.
- The statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished.

4. The amendments have resulted in the cancellation of:

- the description, pages:
- the claims, Nos.:
- the drawings, sheets:

**INTERNATIONAL PRELIMINARY
EXAMINATION REPORT**

International application No. PCT/GB99/04209

5. This report has been established as if (some of) the amendments had not been made, since they have been considered to go beyond the disclosure as filed (Rule 70.2(c)).
(Any replacement sheet containing such amendments must be referred to under item 1 and annexed to this report.)
6. Additional observations, if necessary:

**V. Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability;
citations and explanations supporting such statement**

1. Statement

Novelty (N)	Yes:	Claims
	No:	Claims 1-16
Inventive step (IS)	Yes:	Claims
	No:	Claims 1-16
Industrial applicability (IA)	Yes:	Claims 1-16
	No:	Claims

2. Citations and explanations
see separate sheet

**INTERNATIONAL PRELIMINARY
EXAMINATION REPORT - SEPARATE SHEET**

International application No. PCT/GB99/04209

V

1. The following document is cited in the search report; the numbering will be adhered to in the rest of the procedure :
D1 : US-A-4375357.
2. The present application does not satisfy the criterion set forth in Article 33(2) PCT because the subject-matter of claims 1-16 lacks novelty in view of D1. D1 relates to aqueous inks. The dye is attached to the polymer through several possible groups. Several embodiments consist of a covalent -O- bond (see embodiments 24 and 32 at col. 9 and 14 respectively). The molecular weights can vary between 1.000 and 2.000.000 (average values). The preferred values are between 5.000 and 500.000 (see col. 15, l. 46-52). Since the molecular weights fall within the range of present claim 1, the viscosity will logically follow the same trend. Furthermore, an azo group can be introduced via a diazotisation reaction (see col. 16, lines 4-42). On the other hand, claim 2 is a "product-by-process claim" and, therefore, it is allowable only if the product as such fulfils the requirements for patentability, i. e. if it is new and inventive. The fact that the claimed product has been formed by a certain process does not automatically render said product novel in view of the product prepared by another way.

File

PCT

REQUEST

The undersigned requests that the present international application be processed according to the Patent Cooperation Treaty.

For receiving Office use only

International Application No.

International Filing Date

Name of receiving Office and "PCT International Application"

Applicant's or agent's file reference
(if desired) (12 characters maximum) SMC 60331/WO

Box No. I TITLE OF INVENTION

Ink-Jet Ink Compositions

Box No. II APPLICANT

Name and address: (Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country. The country of the address indicated in this Box is the applicant's State (that is, country) of residence if no State of residence is indicated below.)

Avecia Limited
Hexagon House
Blackley
Manchester M9 8ZS
United Kingdom

This person is also inventor.

Telephone No.
0161 740 1460

Facsimile No.
0161 721 5801

Teleprinter No.

State (that is, country) of nationality:
GB

State (that is, country) of residence:
GB

This person is applicant for the purposes of: all designated States all designated States except the United States of America the United States of America only the States indicated in the Supplemental Box

Box No. III FURTHER APPLICANT(S) AND/OR (FURTHER) INVENTOR(S)

Name and address: (Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country. The country of the address indicated in this Box is the applicant's State (that is, country) of residence if no State of residence is indicated below.)

JAMES, Mark Robert
PO Box 42, Hexagon House
Blackley
Manchester M9 8ZS
United Kingdom

This person is:

applicant only

applicant and inventor

inventor only (If this check-box is marked, do not fill in below.)

State (that is, country) of nationality:
GB

State (that is, country) of residence:
GB

This person is applicant for the purposes of: all designated States all designated States except the United States of America the United States of America only the States indicated in the Supplemental Box

Further applicants and/or (further) inventors are indicated on a continuation sheet.

Box No. IV AGENT OR COMMON REPRESENTATIVE; OR ADDRESS FOR CORRESPONDENCE

The person identified below is hereby/has been appointed to act on behalf of the applicant(s) before the competent International Authorities as:

agent

common representative

Name and address: (Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country.)

SCHMITT Maja
Intellectual Property Group
Avecia Limited
PO Box 42, Hexagon House
Blackley, Manchester M9 8ZS
United Kingdom

Telephone No.

0161 721 1154

Facsimile No.

0161 721 5801

Teleprinter No.

Address for correspondence: Mark this check-box where no agent or common representative is/has been appointed and the space above is used instead to indicate a special address to which correspondence should be sent.

See Notes to the request form

Continuation of Box No. III FURTHER APPLICANTS AND/OR (FURTHER) INVENTORS

If none of the following sub-boxes is used, this sheet should not be included in the request.

Name and address: (Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country. The country of the address indicated in this Box is the applicant's State (that is, country) of residence if no State of residence is indicated below.)

PEARS, David Alan
PO Box 42, Hexagon House
Blackley
Manchester M9 8ZS
United Kingdom

This person is:

- applicant only
 applicant and inventor

inventor only (If this check-box is marked, do not fill in below.)

State (that is, country) of nationality:
GB

State (that is, country) of residence:
GB

This person is applicant for the purposes of:

- all designated States all designated States except the United States of America the United States of America only the States indicated in the Supplemental Box

Name and address: (Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country. The country of the address indicated in this Box is the applicant's State (that is, country) of residence if no State of residence is indicated below.)

DOUBLE, Philip John
PO Box 42, Hexagon House
Blackley
Manchester M9 8ZS
United Kingdom

This person is:

- applicant only
 applicant and inventor
 inventor only (If this check-box is marked, do not fill in below.)

State (that is, country) of nationality:
GB

State (that is, country) of residence:
GB

This person is applicant for the purposes of:

- all designated States all designated States except the United States of America the United States of America only the States indicated in the Supplemental Box

Name and address: (Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country. The country of the address indicated in this Box is the applicant's State (that is, country) of residence if no State of residence is indicated below.)

GREGORY, Peter
PO Box 42, Hexagon House
Blackley
Manchester M9 8ZS
United Kingdom

This person is:

- applicant only
 applicant and inventor
 inventor only (If this check-box is marked, do not fill in below.)

State (that is, country) of nationality:
GB

State (that is, country) of residence:
GB

This person is applicant for the purposes of:

- all designated States all designated States except the United States of America the United States of America only the States indicated in the Supplemental Box

Name and address: (Family name followed by given name; for a legal entity, full official designation. The address must include postal code and name of country. The country of the address indicated in this Box is the applicant's State (that is, country) of residence if no State of residence is indicated below.)

PADGET, John Christopher
21 Fieldway
Frodsham
Cheshire
WA6 6RO
United Kingdom

This person is:

- applicant only
 applicant and inventor
 inventor only (If this check-box is marked, do not fill in below.)

State (that is, country) of nationality:
GB

State (that is, country) of residence:
GB

This person is applicant for the purposes of:

- all designated States all designated States except the United States of America the United States of America only the States indicated in the Supplemental Box

Further applicants and/or (further) inventors are indicated on another continuation sheet.

See Notes to the request form

Box No.V DESIGNATION OF STATES

The following designations are hereby made under Rule 4.9(a) (mark the applicable check-boxes; at least one must be marked).

Regional Patent

- AP ARIPO Patent: GH Ghana, GM Gambia, KE Kenya, LS Lesotho, MW Malawi, SD Sudan, SL Sierra Leone, SZ Swaziland, UG Uganda, ZW Zimbabwe, and any other State which is a Contracting State of the Harare Protocol and of the PCT
- EA Eurasian Patent: AM Armenia, AZ Azerbaijan, BY Belarus, KG Kyrgyzstan, KZ Kazakhstan, MD Republic of Moldova, RU Russian Federation, TJ Tajikistan, TM Turkmenistan, and any other State which is a Contracting State of the Eurasian Patent Convention and of the PCT
- EP European Patent: AT Austria, BE Belgium, CH and LI Switzerland and Liechtenstein, CY Cyprus, DE Germany, DK Denmark, ES Spain, FI Finland, FR France, GB United Kingdom, GR Greece, IE Ireland, IT Italy, LU Luxembourg, MC Monaco, NL Netherlands, PT Portugal, SE Sweden, and any other State which is a Contracting State of the European Patent Convention and of the PCT
- OA OAPI Patent: BF Burkina Faso, BJ Benin, CF Central African Republic, CG Congo, CI Côte d'Ivoire, CM Cameroon, GA Gabon, GN Guinea, GW Guinea-Bissau, ML Mali, MR Mauritania, NE Niger, SN Senegal, TD Chad, TG Togo, and any other State which is a member State of OAPI and a Contracting State of the PCT (if other kind of protection or treatment desired, specify on dotted line)

National Patent (if other kind of protection or treatment desired, specify on dotted line):

- | | | |
|--|--|--------------------------------|
| <input checked="" type="checkbox"/> AE United Arab Emirates | <input checked="" type="checkbox"/> LR Liberia | |
| <input checked="" type="checkbox"/> AL Albania | <input checked="" type="checkbox"/> LS Lesotho | |
| <input checked="" type="checkbox"/> AM Armenia | <input checked="" type="checkbox"/> LT Lithuania | |
| <input checked="" type="checkbox"/> AT Austria | <input checked="" type="checkbox"/> LU Luxembourg | |
| <input checked="" type="checkbox"/> AU Australia | <input checked="" type="checkbox"/> LV Latvia | |
| <input checked="" type="checkbox"/> AZ Azerbaijan | <input checked="" type="checkbox"/> MD Republic of Moldova | |
| <input checked="" type="checkbox"/> BA Bosnia and Herzegovina | <input checked="" type="checkbox"/> MG Madagascar | |
| <input checked="" type="checkbox"/> BB Barbados | <input checked="" type="checkbox"/> MK The former Yugoslav Republic of Macedonia | |
| <input checked="" type="checkbox"/> BG Bulgaria | <input checked="" type="checkbox"/> MN Mongolia | |
| <input checked="" type="checkbox"/> BR Brazil | <input checked="" type="checkbox"/> MW Malawi | |
| <input checked="" type="checkbox"/> BY Belarus | <input checked="" type="checkbox"/> MX Mexico | |
| <input checked="" type="checkbox"/> CA Canada | <input checked="" type="checkbox"/> NO Norway | |
| <input checked="" type="checkbox"/> CH and LI Switzerland and Liechtenstein | <input checked="" type="checkbox"/> NZ New Zealand | |
| <input checked="" type="checkbox"/> CN China | <input checked="" type="checkbox"/> PL Poland | |
| <input checked="" type="checkbox"/> CU Cuba | <input checked="" type="checkbox"/> PT Portugal | |
| <input checked="" type="checkbox"/> CZ Czech Republic | <input checked="" type="checkbox"/> RO Romania | |
| <input checked="" type="checkbox"/> DE Germany | <input checked="" type="checkbox"/> RU Russian Federation | |
| <input checked="" type="checkbox"/> DK Denmark | <input checked="" type="checkbox"/> SD Sudan | |
| <input checked="" type="checkbox"/> EE Estonia | <input checked="" type="checkbox"/> SE Sweden | |
| <input checked="" type="checkbox"/> ES Spain | <input checked="" type="checkbox"/> SG Singapore | |
| <input checked="" type="checkbox"/> FI Finland | <input checked="" type="checkbox"/> SI Slovenia | |
| <input checked="" type="checkbox"/> GB United Kingdom | <input checked="" type="checkbox"/> SK Slovakia | |
| <input checked="" type="checkbox"/> GD Grenada | <input checked="" type="checkbox"/> SL Sierra Leone | |
| <input checked="" type="checkbox"/> GE Georgia | <input checked="" type="checkbox"/> TJ Tajikistan | |
| <input checked="" type="checkbox"/> GH Ghana | <input checked="" type="checkbox"/> TM Turkmenistan | |
| <input checked="" type="checkbox"/> GM Gambia | <input checked="" type="checkbox"/> TR Turkey | |
| <input checked="" type="checkbox"/> HR Croatia | <input checked="" type="checkbox"/> TT Trinidad and Tobago | |
| <input checked="" type="checkbox"/> HU Hungary | <input checked="" type="checkbox"/> UA Ukraine | |
| <input checked="" type="checkbox"/> ID Indonesia | <input checked="" type="checkbox"/> UG Uganda | |
| <input checked="" type="checkbox"/> IL Israel | <input checked="" type="checkbox"/> US United States of America | |
| <input checked="" type="checkbox"/> IN India | <input checked="" type="checkbox"/> UZ Uzbekistan | |
| <input checked="" type="checkbox"/> IS Iceland | <input checked="" type="checkbox"/> VN Viet Nam | |
| <input checked="" type="checkbox"/> JP Japan | <input checked="" type="checkbox"/> YU Yugoslavia | |
| <input checked="" type="checkbox"/> KE Kenya | <input checked="" type="checkbox"/> ZA South Africa | |
| <input checked="" type="checkbox"/> KG Kyrgyzstan | <input checked="" type="checkbox"/> ZW Zimbabwe | |
| <input checked="" type="checkbox"/> KP Democratic People's Republic of Korea | Check-boxes reserved for designating States which have become party to the PCT after issuance of this sheet: | |
| <input checked="" type="checkbox"/> KR Republic of Korea | <input checked="" type="checkbox"/> CR Costa Rica | DM Dominica |
| <input checked="" type="checkbox"/> KZ Kazakhstan | <input checked="" type="checkbox"/> MA Morocco | TZ United Republic of Tanzania |
| <input checked="" type="checkbox"/> LC Saint Lucia | | |
| <input checked="" type="checkbox"/> LK Sri Lanka | | |

Precautionary Designation Statement: In addition to the designations made above, the applicant also makes under Rule 4.9(b) all other designations which would be permitted under the PCT except any designation(s) indicated in the Supplemental Box as being excluded from the scope of this statement. The applicant declares that those additional designations are subject to confirmation and that any designation which is not confirmed before the expiration of 15 months from the priority date is to be regarded as withdrawn by the applicant at the expiration of that time limit. (Confirmation of a designation consists of the filing of a notice specifying that designation and the payment of the designation and confirmation fees. Confirmation must reach the receiving Office within the 15-month time limit.)

See Notes to the request form

Supplemental Box*If the Supplemental Box is not used, this sheet should not be included in the request.*

1. If, in any of the Boxes, **the space is insufficient** to furnish all the information: in such case, write "Continuation of Box No." [indicate the number of the Box] and furnish the information in the same manner as required according to the captions of the Box in which the space was insufficient, in particular:

- (i) if **more than two persons are involved as applicants and/or inventors** and no "continuation sheet" is available: in such case, write "Continuation of Box No. III" and indicate for each additional person the same type of information as required in Box No. III. The country of the address indicated in this Box is the applicant's State (that is, country) of residence if no State of residence is indicated below;
- (ii) if, in Box No. II or in any of the sub-boxes of Box No. III, the indication "**the States indicated in the Supplemental Box**" is checked: in such case, write "Continuation of Box No. II" or "Continuation of Box No. III" or "Continuation of Boxes No. II and No. III" (as the case may be), indicate the name of the applicant(s) involved and, next to (each) such name, the State(s) (and/or, where applicable, ARIPO, Eurasian, European or OAPI patent) for the purposes of which the named person is applicant;
- (iii) if, in Box No. II or in any of the sub-boxes of Box No. III, **the inventor or the inventor/applicant is not inventor for the purposes of all designated States or for the purposes of the United States of America**: in such case, write "Continuation of Box No. II" or "Continuation of Box No. III" or "Continuation of Boxes No. II and No. III" (as the case may be), indicate the name of the inventor(s) and, next to (each) such name, the State(s) (and/or, where applicable, ARIPO, Eurasian, European or OAPI patent) for the purposes of which the named person is inventor;
- (iv) if, in addition to the agent(s) indicated in Box No. IV, there are **further agents**: in such case, write "Continuation of Box No. IV" and indicate for each further agent the same type of information as required in Box No. IV;
- (v) if, in Box No. V, the name of any State (or OAPI) is accompanied by the indication "**patent of addition**," or "**certificate of addition**," or if, in Box No. V, the name of the United States of America is accompanied by an indication "**continuation**" or "**continuation-in-part**": in such case, write "Continuation of Box No. V" and the name of each State involved (or OAPI), and after the name of each such State (or OAPI), the number of the parent title or parent application and the date of grant of the parent title or filing of the parent application;
- (vi) if, in Box No. VI, there are **more than three earlier applications whose priority is claimed**: in such case, write "Continuation of Box No. VI" and indicate for each additional earlier application the same type of information as required in Box No. VI;
- (vii) if, in Box No. VI, **the earlier application is an ARIPO application**: in such case, write "Continuation of Box No. VI", specify the number of the item corresponding to that earlier application and indicate at least one country party to the Paris Convention for the Protection of Industrial Property for which that earlier application was filed.

2. If, with regard to the **precautionary designation statement** contained in Box No. V, the applicant wishes to exclude any State(s) from the scope of that statement: in such case, write "Designation(s) excluded from precautionary designation statement" and indicate the name or two-letter code of each State so excluded.

3. If the applicant claims, in respect of any designated Office, the benefits of provisions of the national law concerning **non-prejudicial disclosures or exceptions to lack of novelty**: in such case, write "Statement concerning non-prejudicial disclosures or exceptions to lack of novelty" and furnish that statement below.

Continuation of Box IV

FAWKES, David Melville

MAYALL, John

NELSON, Michael Andrew

PUGSLEY, Roger Graham

REVELL, Christopher

SCHMITT, Maja

SHELLER, Alan

All of Intellectual Property Group, Avecia Limited, PO Box 42, Hexagon House, Blackley, Manchester M9 8ZS, United Kingdom

LOCKE, Timothy John

of Intellectual Property Group, Avecia Limited, PO Box 2, Belasis Avenue, Billingham, Cleveland TS23 1YN, United Kingdom

Box No. VI PRIORITY CLAIM		<input type="checkbox"/> Further priority claims are indicated in the Supplemental Box.		
Filing date of earlier application (day/month/year)	Number of earlier application	Where earlier application is:		
		national application: country	regional application: regional Office	international application: receiving Office
item (1) 21 December 1998 (21/12/98)	9827894.8	GB		
item (2)				
item (3)				

The receiving Office is requested to prepare and transmit to the International Bureau a certified copy of the earlier application(s) (only if the earlier application was filed with the Office which for the purposes of the present international application is the receiving Office) identified above as item(s): 1

* Where the earlier application is an ARIPO application, it is mandatory to indicate in the Supplemental Box at least one country party to the Paris Convention for the Protection of Industrial Property for which that earlier application was filed (Rule 4.10(b)(ii)). See Supplemental Box.

Box No. VII INTERNATIONAL SEARCHING AUTHORITY

Choice of International Searching Authority (ISA) (if two or more International Searching Authorities are competent to carry out the international search, indicate the Authority chosen; the two-letter code may be used): Request to use results of earlier search; reference to that search (if an earlier search has been carried out by or requested from the International Searching Authority):

Date (day/month/year) Number Country (or regional Office)

ISA / EPO

Box No. VIII CHECK LIST; LANGUAGE OF FILING

This international application contains the following number of sheets:	This international application is accompanied by the item(s) marked below:
request : 05	1. <input checked="" type="checkbox"/> fee calculation sheet
description (excluding sequence listing part) : 26	2. <input type="checkbox"/> separate signed power of attorney
claims : 02	3. <input type="checkbox"/> copy of general power of attorney; reference number, if any:
abstract : 01	4. <input type="checkbox"/> statement explaining lack of signature
drawings : --	5. <input type="checkbox"/> priority document(s) identified in Box No. VI as item(s):
sequence listing part of description : 00	6. <input type="checkbox"/> translation of international application into (language):
Total number of sheets : 34	7. <input type="checkbox"/> separate indications concerning deposited microorganism or other biological material
	8. <input type="checkbox"/> nucleotide and/or amino acid sequence listing in computer readable form
	9. <input type="checkbox"/> other (specify):

Figure of the drawings which should accompany the abstract:

Language of filing of the international application: ENGLISH

Box No. IX SIGNATURE OF APPLICANT OR AGENT

Next to each signature, indicate the name of the person signing and the capacity in which the person signs (if such capacity is not obvious from reading the request).

For Avecia Limited JAMES Mark Robert, PEARS David Alan, DOUBLE Philip John,
GREGORY Peter, PADGET John Christopher

SCHMITT Maja

For receiving Office use only		
1. Date of actual receipt of the purported international application: 3. Corrected date of actual receipt due to later but timely received papers or drawings completing the purported international application: 4. Date of timely receipt of the required corrections under PCT Article 11(2): 5. International Searching Authority (if two or more are competent): ISA /		2. Drawings: <input type="checkbox"/> received: <input type="checkbox"/> not received:
6. <input type="checkbox"/> Transmittal of search copy delayed until search fee is paid.		

For International Bureau use only

Date of receipt of the record copy by the International Bureau:

See Notes to the request form

*REPLACED BY
ART 3A N*

In one embodiment the olefinic water-dissipatable polymer may be prepared by polymerising an acrylic oligomer having water-dispersing groups and at least one olefinically unsaturated terminal group in the presence of one or more olefinically unsaturated monomers having a hydroxy functional group or a group which is 5 convertible to a hydroxy functional group, and optionally one or more olefinically unsaturated monomers which are free from water-dispersing groups and/or one or more olefinically unsaturated monomers having water-dispersing groups.

Alternatively an acrylic oligomer with at least one olefinically unsaturated terminal group and which is free from water-dispersing groups may be polymerised in the 10 presence of one or more olefinically unsaturated monomers having a hydroxy functional group or a group which is convertible to a hydroxy functional group and one or more olefinically unsaturated monomers having water-dispersing groups.

Preferred polymerisation methods include solution polymerisation, emulsion polymerisation, suspension polymerisation and solution/dispersion polymerisation and 15 such general methods as are well known in the art. More preferably aqueous or non-aqueous solution polymerisation and emulsion polymerisation is used and most preferably solution polymerisation is used.

If desired, an initiator may be used to assist the water-dissipatable olefinic 20 polymer formation. Suitable initiators are free-radical generators. Examples of catalysts include azobis compounds, peroxides, hydroperoxides, redox catalysts, etc., for example, potassium persulfate, ammonium persulfate, tert-butyl peroctoate, benzoyl peroxide, isopropyl percarbonate, 2,4-dichlorobenzoyl peroxide, methyl ethyl ketone peroxide, cumene hydroperoxide, dicumyl peroxide, azobisisobutyronitrile, azobis(2-amidino-propane)hydrochloride and the like.

25 Typically 0.05 to 5% by weight of initiator is used relative to the total weight of the monomers. Preferably the polymerisation is performed in the presence of an emulsifying agent.

The molecular weight of the olefinic water-dissipatable polymer may be controlled by the addition of chain transfer agents and/or through the adjustment of the 30 ratio of the concentration of monomers relative to the concentration of initiator during the course of the polymerisation. Typical chain transfer agents are thiols, halocarbons and cobalt macrocycles.

When the water-dissipatable polymer is a polyester or polyurethane it may be prepared by conventional techniques, for example as described in PCT/GB99/00656 35 (polyurethanes) or PCT/GB98/01583 (polyesters) using a monomer carrying a protected hydroxy functional group to form the water-dissipatable polymer followed by removal of the protecting group prior to reaction with a colorant, a colorant precursor, or a bridging compound to give a covalent -O-link.

When the water-dissipatable polymer is prepared by the polymerisation of

The ink preferably has a pH from 3 to 11, more preferably from 4 to 10. The pH selected will depend to some extent on the desired cation for colorant and the materials used to construct the ink jet printer head. The desired pH may be obtained by the addition of an acid, base or a pH buffer. Where a base is used this is preferably the same base as was used to neutralise any anionic dispersing group during the preparation of the water-dissipatable polymer of the invention.

5 The viscosity of the ink is preferably less than 20cp, more preferably less than 15cp, especially less than 10cp, at 20°C.

Preferably the ink has been filtered through a filter having a mean pore size 10 below 10 µm, preferably below 5 µm, more preferably below 2µm, especially below 0.45 µm. In this way particulate matter is removed which could otherwise block fine nozzles in an ink jet printer.

15 Preferably the ink contains less than 500 ppm, more preferably less than 250 ppm, especially less than 100 ppm of in total of divalent and trivalent metal ions.

The inks of the present invention have the advantage that they are suitable not only for the use in piezoelectric ink jet printers but also in thermal and continuous ink jet printers. Many other inks based on polymers work poorly or even not at all in thermal ink 20 jet printers.

Inks of the present invention form discrete droplets on the substrate with little tendency for diffusing. Consequently sharp images with excellent print quality and little if any bleed between colours printed side by side can be obtained. Furthermore the inks show good storage stability, wet and light fastness and fastness to both acidic and alkaline highlighter pens.

25 A third aspect of the invention provides a process for printing an image on a substrate comprising applying thereto an ink according to the second aspect of the present invention by means of an ink jet printer.

The ink jet printer preferably applies the ink to the substrate in the form of droplets which are ejected through a small nozzle onto the substrate. Preferred ink jet printers are piezoelectric ink jet printers and thermal ink jet printers. In thermal ink jet printers, 30 programmed pulses of heat are applied to the ink in a reservoir by means of a resistor adjacent to the nozzle, thereby causing the ink to be ejected in the form of small droplets directed towards the substrate during relative movement between the substrate and the nozzle. In piezoelectric ink jet printers the oscillation of a small crystal causes ejection of the ink from the nozzle.

35 The substrate is preferably a paper, plastic, or textile material, more preferably a paper, an overhead projector slide or a textile material, especially paper.

Preferred papers are plain, coated or treated papers which may have an acid, alkaline or neutral character. Most preferably the substrate is a coated paper.

40 According to a fourth feature of the invention there is provided an ink jet printer cartridge, optionally refillable, containing an ink as hereinbefore defined.

CLAIMS

1. A water-dissipatable polymer having colorant attached thereto through a covalent -O- link.

5

2. A water-dissipatable polymer according to claim 1 obtainable by the reaction of a water-dissipatable polymer with pendant hydroxy functional groups with a colorant having a functional group capable of reacting with hydroxy functional groups.

10

3. A water-dissipatable polymer according to claim 1 wherein the colorant is attached thereto by means of a reaction between a hydroxy group on the polymer with a colorant precursor thereby forming a covalent bond therebetween and subsequently converting the colorant precursor to a colorant

15

4. A water-dissipatable polymer according to claim 1 wherein the colorant is attached thereto by means of a reaction between a hydroxy group on the polymer with a bridging compound thereby forming a covalent bond therebetween and subsequently reacting the bridging compound with a colorant or colorant precursor.

20

5. A water-dissipatable polymer according to claim 4 wherein the colorant precursor is converted to a colorant by a process comprising a diazotisation reaction.

6. A water-dissipatable polymer according to claim 5 wherein the diazotisation reaction comprises the steps:

25

(i) diazotising an amino group in the colorant precursor using a diazotising agent; and
(ii) coupling the product of step (i) with a coupling component forming an azo group therebetween.

30

7. A water-dissipatable polymer according to anyone of the preceding claims wherein the polymer is an olefinic polymer.

35

8. A water-dissipatable polymer according to claim 7 wherein the olefinic polymer is obtainable from the polymerisation of one or more olefinically unsaturated monomers having water-dispersing groups, and one or more olefinically unsaturated monomers having hydroxy functional groups optionally in the presence of one or more olefinically unsaturated monomers which are free from water-dispersing and hydroxy functional groups.

9. A water-dissipatable polymer according to any one of the preceding claims wherein the water-dissipatable polymer has a Mn less than 25,000.

10. An ink comprising the components:

- 5 (a) a water-dissipatable polymer according to any one of claims 1 to 9; and
(b) a liquid medium.

11. An ink according to claim 10 wherein component (a) is completely dissipated in component (b).

10 12. An ink according to claim 10 or 11 which comprises from 0.5 to 50 parts of component (a) and from 50 to 99.5 parts of component (b), wherein all parts are by weight and the number of parts of (a) + (b) = 100.

15 13. An ink according to claim 10, 11 or 12 wherein component (b) comprises water and an organic solvent.

14. An ink according to claim 13 where component (b) comprises from 40 to 95 parts of water and from 2 to 60 parts of water-miscible organic solvent.

20 15. An ink according to any one of claims 10 to 14 having a viscosity less than 20 cp at 20°C.

16. An ink according to any one of claims 11 to 15 for use in an ink jet printer.

25 17. A process for forming an image on a substrate comprising applying thereto an ink using an ink jet printer, characterised in that the ink is as defined in any one of claims 11 to 15.

30 18. A paper or an overhead projector slide printed with an ink as defined in any one of claims 11 to 15.

19. An ink jet printer cartridge, optionally refillable, containing an ink as defined in any one of claims 11 to 15.

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(54) Title: INK-JET INK COMPOSITIONS			
(57) Abstract			
A water-dissipatable polymer having colorant attached thereto through a covalent -O-link and an ink comprising the water-dissipatable polymer and a liquid medium.			

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INK-JET INK COMPOSITIONS

This invention relates to coloured water-dissipatable polymers, to inks containing the coloured water-dissipatable polymers and to their use in ink jet printing.

Ink jet printing methods involve a non-impact printing technique for printing an image onto a substrate using ink droplets ejected through a fine nozzle onto a substrate without bringing the nozzle into contact with the substrate.

There are many demanding performance requirements for colorants and inks used in ink jet printing. For example they desirably provide sharp, non-feathered images having good water-fastness, light-fastness and optical density. The inks are often required to dry quickly when applied to a substrate to prevent smudging, but they should not form a crust over the tip of an ink jet nozzle because this will stop the printer from working. The inks should also be stable to storage over time without decomposing or forming a precipitate which could block the fine nozzle. The most popular ink jet printers are thermal and piezoelectric ink jet printers.

There is a need for inks which are suitable for both thermal and piezo ink jet printers, have high colour strength and produce images having a high light-fastness and water-fastness when printed on a substrate.

We have surprisingly found that the coloration of water-dissipatable polymers having hydroxy functional groups by reacting the hydroxy functional groups with a colorant, a bridging group for a colorant or a colorant precursor and further reaction of the bridging compound with a colorant or colorant precursor and subsequent conversion of the colorant precursor to a colorant, gives a coloured water-dissipatable polymer which is suitable for use in inks for thermal and piezo ink jet printers.

According to a first aspect of the present invention there is provided a water-dissipatable polymer having colorant attached thereto through a covalent -O- link.

A -O- link may be exemplified by but is not limited to the following links such as an ether link (R^1-O-R^2), an ester link ($R^1-O-C(O)-R^2$) and a phosphate ester link ($R^1-O-P(O)(OH)-R^2$), where R^1 represents the water-dissipatable polymer and R^2 represents the colorant.

A water-dissipatable polymer of the invention is obtainable by attaching a colorant to a water-dissipatable polymer having hydroxy functional groups by means of a reaction between the hydroxy functional groups on the polymer with a colorant having a functional group capable of reacting with the hydroxy functional group.

The colorant may also be attached to the water-dissipatable polymer by means of a reaction between a hydroxy group on the polymer with a colorant precursor thereby forming a covalent bond therebetween and subsequently converting the colorant precursor to a colorant.

Alternatively, colorants may be grafted to the water-dissipatable polymer via a bridging compound. For example, colorant may be attached to the water-dissipatable polymer by means of a reaction between the hydroxy functional group on the water-dissipatable polymer with a bridging compound thereby forming a covalent bond therebetween and subsequently reacting the bridging compound with a colorant or colorant precursor. The bridging agent may be a di-, tri-, tetra- or polyfunctional structure, and examples include, but are not limited to bis alkyl halides, tris dialkyl halides, bis acid chlorides, tris diacid chlorides, bis vinyl sulphones, tris divinyl sulphones, mixtures of alkyl halides and acid chlorides, michael acceptors, cyanuric chloride and related reactive 1,3,5-triazines, other reactive heterocyclic halides and aromatic halides. Most preferably cyanuric chloride is used.

The water-dissipatable polymer of the invention is preferably prepared by condensing a water-dissipatable polymer having hydroxy functional groups with a colorant having a functional group reactive towards the hydroxy functional groups. Such functional groups are described above. Up to 100%, preferably at least 95%, more preferably at least 90%, most preferably at least 85% of the hydroxy functional groups are reacted with the colorant. The condensation is performed by preparing a solution or suspension of a water-dissipatable polymer having hydroxy functional groups in an aqueous and/or non-aqueous solvent. Preferably the condensation is performed at a pH of 5 to 14, more preferably of 6 to 13, especially of 7 to 12. The condensation is preferably performed in the presence of an inorganic or organic base. Preferred inorganic bases are NaOH, KOH, Na₂CO₃, K₂CO₃. Preferred organic bases are trialkyl amines, 1,5-diazabicyclo[4.3.0]non-5-ene (DBN), 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), and 1,4-diazabicyclo[2.2.2]octane (DABCO). Subsequently an aqueous solution of a colorant is added to the suspension and the mixture is stirred until the reaction is complete.

Alternatively a non-aqueous grafting reaction can be used to react the water-dissipatable polymer having hydroxy functional groups with a colorant. The colorant and polymer are stirred in a non-aqueous solvent with a base (either homogeneous or heterogeneous) and heated as required to complete the reaction. In the case of ester formation, for example reacting an acid functionalised colorant (e.g. phosphoric acid functionalised) and the water-dissipatable polymer having hydroxy functional groups, conditions are required to remove the generated water either physically (e.g. by azeotroping, molecular sieves) or chemically using a dehydrating agent such as dicyclohexylcarbodiimide or dicyandiamide. Acid catalysts such as p-toluenesulphonic acid or sulphuric acid may also be employed.

The water-dissipatable polymer of the invention may be isolated from the aqueous system by either acidification and filtration; dilution with a water miscible solvent and filtration; salting out with organic salts or solutions of organic salts or combinations of these methods. Suitable salts include sodium chloride, ammonium

chloride, sodium sulphate and lithium chloride. Alternatively the mixture is acidified until the water-dissipatable polymer of the invention precipitates out, or the solvent is evaporated or the solvent is diluted with water until the water-dissipatable polymer of the invention precipitates out.

5 Alternatively the water-dissipatable polymer of the present invention may be purified by ion-exchange methods on cationic resins. Other options include the removal of low molecular weight materials such as co-solvents used for the polymerisation, low molecular weight salts, impurities and free monomers by ultra-filtration, osmosis, reverse osmosis, dialysis, ultra-filtration or a combination thereof, followed by evaporation of the water.

10 Preferably the number average molecular weight (M_n) of the water-dissipatable polymer used to make the polymer of the invention is less than 25,000, more preferably is less than 20,000, especially less than 15,000. The M_n of the polymer may be measured by gel permeation chromatography ("gpc").

15 The gpc method used for determining M_n preferably comprises applying the polymer to a chromatography column packed with cross-linked polystyrene/divinyl benzene, eluting the column with tetrahydrofuran at a temperature of 40°C and assessing the M_n of the polymer compared to a number of a polystyrene standards of a known M_n . Suitable cross-linked polystyrene/divinyl benzene chromatography columns 20 are commercially available from Polymer Laboratories.

As an alternative to the gpc method for determining M_n , the M_n may be determined using for example by multi-angle light scattering (MALLS).

The water-dissipatable polymer may be a copolymer, for example a random, alternating or block copolymer, preferably a random copolymer.

25 The water-dissipatable olefinic polymer may be a polyurethane, polyester or an olefinic polymer. Preferably the water-dissipatable polymer is an olefinic polymer. An olefinic polymer is a polymer obtainable from the polymerisation of one or more olefinically unsaturated monomers.

30 The water-dissipatable olefinic polymer is preferably obtainable from the polymerisation of one or more olefinically unsaturated monomers having hydroxy functional groups, and one or more olefinically unsaturated monomers having water-dispersing groups optionally in the presence of one or more olefinically unsaturated monomers which are free from water-dispersing groups.

35 Preferred olefinically unsaturated monomers having hydroxy functional group(s) include, but are not limited to, hydroxy-functional esters of acrylic acid, methacrylic acid, maleic acid, or fumaric acid. Examples of such monomers include hydroxy functional alkyl (preferably 1 to 18C) (meth)acrylates such as 2-hydroxy ethylacrylate, 2-hydroxy ethylmethacrylate, 2-hydroxy propylacrylate, 3-hydroxy propylacrylate, 2-hydroxy propylmethacrylate, 3-hydroxy propylmethacrylate, 4-hydroxy butylacrylate, 4-hydroxy butylmethacrylate, hydroxy stearylacrylate, hydroxy stearylmethacrylate; dihydroxy alkyl

(preferably 1 to 6C) adducts of maleic acid, fumaric acid, and phthalic acid; polyethylene oxide or polypropylene oxide functionalised hydroxyl functional (meth)acrylate such as the commercially available material known as BISOMER PPM5S, BISOMER PPM6E (International Specialty Chemicals); Caprolactone acrylate monomers such as the commercial available material known as TONE M100 Monomer (Union Carbide). Other examples include (4-hydroxymethyl cyclohexyl) - methylacrylate (Mitsubishi Chemical); and Blemmer PE-90, Blemmer PE-200, and Blemmer PE-350 (polyethylene glycol methacrylates of molecular weights 163-173, 261-303 and 387-468 respectively); Blemmer 70 PEP-350B ($\text{CH}_2=\text{C}(\text{CH}_3)-\text{C}(=\text{O})-(\text{EO})_n-\text{H}$ where EO is polyethylene oxide, PO is polypropylene oxide and the molecular weight is about 450); and Blemmer-GLM (glycerol dimethacrylate) (all Nippon Oil and Fats Co.); N-methylol acrylamide, glycerol monomethacrylate and trimethylol propane mono methacrylate.

Olefinically unsaturated monomers having a hydroxy functional group also includes olefinically unsaturated monomers having a group which is convertible to a hydroxy functional group and include but are not limited to vinyl acetate, vinyl benzoate, vinyl benzyl chloride, vinyl bromide and vinyl chloride.

Water-dispersing groups provide the facility of self-dispersibility and solubility to the polymer in ink media, especially in water. The water-dispersing groups may be ionic, non-ionic or a mixture of ionic and non-ionic water-dispersing groups. Preferred ionic water-dispersing groups include basic amine groups, cationic quaternary ammonium groups and acid groups, for example phosphoric acid groups, sulphonic acid groups and carboxylic acid groups.

The water-dispersing groups may be incorporated into the polymer in the form of monomers or oligomers bearing the appropriate water-dispersing groups. One may also react a polymer which is not water-dissipatable with monomers or oligomers which make the polymer water-dissipatable.

The nature and level of water-dispersing groups in the polymer influences whether a solution, dispersion, emulsion or suspension is formed on dissipation of the water-dissipatable polymer.

The water-dispersing group content of the water-dissipatable polymer may vary within wide limits but is preferably sufficient to make the water-dissipatable polymer form stable ink-jet printing inks in water and aqueous media.

The acid water-dispersing groups may be subsequently fully or partially neutralised with a base containing a cationic charge to give a salt. If the acid water-dispersing groups are used in combination with a non-ionic water-dispersing group, neutralisation may not be required. The conversion of any free acid groups into the corresponding salt may be effected during the preparation of the water-dissipatable polymer and/or during the preparation of an ink from the water-dissipatable polymer.

Preferably the base used to neutralise any acid water-dispersing groups is ammonia, an amine or an inorganic base. Suitable amines are tertiary amines, for

example triethylamine or triethanolamine. Suitable inorganic bases include alkaline hydroxides and carbonates, for example lithium hydroxide, sodium hydroxide, or potassium hydroxide. A quaternary ammonium hydroxide, for example $N^+(CH_3)_4OH^-$, can also be used. Generally a base is used which gives the required counter ion desired for the ink which is prepared from the polymer. For example, suitable counter ions include Li^+ , Na^+ , K^+ , NH_4^+ and substituted ammonium salts.

Preferred olefinically unsaturated monomers providing ionic water-dispersing groups include acrylic acid, methacrylic acid, itaconic acid, maleic acid, monoalkyl itaconates (for example, monomethyl maleate, monoethyl maleate, monobutyl maleate and monoocetyl maleate), citraconic acid, styrenesulfonic acid, vinylbenzylsulfonic acid, vinylsulfonic acid, acryloyloxyalkyl sulfonic acids (for example, acryloyloxyethyl sulfonic acid, acryloyloxyethyl sulfonic acid, acryloyloxypropyl sulfonic acid and acryloyloxybutyl sulfonic acid), methacryloyloxyethyl sulfonic acid, methacryloyloxypropyl sulfonic acid and methacryloyloxybutyl sulfonic acid), 2-acrylamido-2-alkylalkane sulfonic acids (for example, 2-acrylamido-2-methylethanesulfonic acid, 2-acrylamido-2-methylpropanesulfonic acid and 2-acrylamido-2-methylbutane sulfonic acid), 2-methacrylamido-2-alkylalkane sulfonic acids (for example, 2-methacrylamido-2-methylethanesulfonic acid, 2-methacrylamido-2-methylpropanesulfonic acid and 2-methacrylamido-2-methylbutanesulfonic acid), mono-(acryloyloxyalkyl)phosphates (for example, mono(acryloyloxyethyl)phosphate and mono(3-acryloyloxypropyl)phosphates) and mono(methacryloyloxyalkyl)phosphates (for example, mono(methacryloyloxyethyl)phosphate and mono(3-methacryloyloxypropyl)phosphate).

Non-ionic water-dispersing groups may be in-chain, pendant or terminal groups. Preferably non-ionic water-dispersing groups are pendant polyoxyalkylene groups, more preferably polyoxyethylene groups. The non-ionic water-dispersing groups may be introduced into the water-dissipatable polymer in the form of a compound bearing non-ionic water-dispersing groups and at least one (although preferably only one) copolymerisable olefinically unsaturated group.

Preferred olefinically unsaturated monomers providing non-ionic water-dispersing groups include alkoxy polyethylene glycol (meth)acrylates, preferably having a number average molecular weight of from 350 to 2000. Examples of such monomers which are commercially available include ω -methoxypolyethylene glycol (meth)acrylate and diethylene glycol mono vinyl ether.

In addition to the water-dissipatable polymer comprising olefinically unsaturated monomers having a hydroxy functional group or a group which is convertible to a hydroxy functional group, and one or more olefinically unsaturated monomers having water-dispersing groups, the water-dissipatable polymer may also contain one or more

olefinically unsaturated monomers which are free from water-dispersing groups and/or hydroxy functional groups.

Preferred olefinically unsaturated monomers which are free from water-dispersing groups include alkyl(meth)acrylates, optionally substituted styrenes, methacrylamides, allyl compounds, dienes, vinyl ethers, vinyl ketones, vinyl halides, vinylidene halides, olefins and unsaturated nitriles.

Preferred alkyl(meth)acrylates contain less than twenty carbon atoms. Examples include methyl acrylate, ethyl acrylate, n-propyl acrylate, isopropyl acrylate, n-butyl acrylate, isobutyl, sec-butyl acrylate, amyl acrylate, hexyl acrylate, 2-ethylhexyl acrylate, 10 octyl acrylate, tert-octyl acrylate, 2-phenoxyethyl acrylate, 2-chloroethyl acrylate, 2-bromoethyl acrylate, 4-chlorobutyl acrylate, cyanoethyl acrylate, 2-acetoxyethyl acrylate, dimethylaminoethyl acrylate, benzyl acrylate, methoxybenzyl acrylate, 2-chlorocyclohexyl acrylate, acylate, cyclohexyl acylate, furfuryl acrylate, tetrahydrofurfuryl acrylate, phenyl acrylate, 5-hydroxypentyl acrylate, 2,2-dimethyl-3-hydroxypropyl acrylate, 2-methoxyethyl acrylate, 3-methoxybutyl acrylate, 2-ethoxyethyl acrylate, 2-isopropoxyethyl acrylate, 2-butoxyethyl acrylate, 2-(2-methoxyethoxy)ethyl acrylate, 2-(2-butoxyethoxy)ethyl acrylate, 1-bromo-2-methoxyethyl acrylate, 1,1-dichloro-2-ethoxyethyl acrylate, methyl methacrylate, ethyl methacrylate, n-propyl methacrylate, isopropyl methacrylate, n-butyl methacrylate, isobutyl methacrylate, sec-butyl methacrylate, amyl methacrylate, hexyl methacrylate, cyclohexyl methacrylate, benzylmethacrylate, chlorobenzyl methacrylate, octyl methacrylate, N-ethyl-N-phenylaminoethyl methacrylate, 2-(3-phenylpropyloxy)ethyl methacrylate, dimethylaminophenoxyethyl methacrylate and furfuryl methacrylate. Aromatic examples include but are not limited to 4-alkyl phenylacrylate or methacrylate, phenyl methacrylate, phenyl acrylate, and β-naphthyl methacrylate,

Preferred optionally substituted styrenes include styrene, methylstyrene, dimethylstyrene, trimethylstyrene, ethylstyrene, diethylstyrene, isopropylstyrene, butylstyrene, hexylstyrene, cyclohexylstyrene, decylstyrene, chloromethylstyrene, trifluoromethylstyrene, ethoxymethylstyrene, acetoxyethylstyrene, methoxystyrene, 4-methoxy-3-methylstyrene, dimethoxystyrene, chlorostyrene, dichlorostyrene, 30 trichlorostyrene, tetrachlorostyrene, pentachlorostyrene, bromostyrene, dibromostyrene, iodostyrene, trifluorostyrene and 2-bromo-4-tri-fluoromethylstyrene.

Preferred methacrylamides contain less than 12 carbon atoms. Examples include methylmethacrylamide, tert-butylmethacrylamide, tert-octylmethacrylamide, benzylmethacrylamide, cyclohexylmethacrylamide, phenylmethacrylamide, dimethylmethacrylamide, dipropylmethacrylamide, hydroxyethyl-N-methylmethacrylamide, N-methylphenylmethacrylamide, N-ethyl-N-phenylmethacrylamide and methacrylhydrazine.

Preferred allyl compounds include allyl acetate, allyl caproate, allyl caprylate, allyl laurate, allyl palmitate, allyl stearate, allyl benzoate, allyl acetoacetate, allyl lactate, allyloxyethanol, allyl butyl ether and allyl phenyl ether.

Preferred vinyl ethers contain less than 20 carbon atoms. Examples include methyl vinyl ether, butyl vinyl ether, hexyl vinyl ether, octyl vinyl ether, decyl vinyl ether, ethylhexyl vinyl ether, methoxyethyl vinyl ether, ethoxyethyl vinyl ether, chloroethyl vinyl ether, 1-methyl-2,2-dimethylpropyl vinyl ether, 2-ethylbutyl vinyl ether, hydroxyethyl vinyl ether and dimethylaminoethyl vinyl ether.

Preferred vinyl ketones contain less than 12 carbon atoms. Examples include methyl vinyl ketone, phenyl vinyl ketone and methoxyethyl vinyl ketone.

Preferred vinyl halides include vinyl chloride, vinylidene chloride and chlorotrifluoroethylene.

Preferred olefins include unsaturated hydrocarbons having less than 20 carbon atoms. Examples include dicyclopentadiene, ethylene, propylene, 1-butene, 1-pentene, 1-hexene, 4-methyl-1-pentene, 1-heptene, 1-octene, 1-decene, 5-methyl-1-nonene, 5,5-dimethyl-1-octene, 4-methyl-1-hexene, 4,4-dimethyl-1-pentene, 5-methyl-1-hexene, 4-methyl-1-heptene, 5-methyl-1-heptene, 4,4-dimethyl-1-hexene, 5,5,6-trimethyl-1-heptene, 1-dodecene and 1-octadecene.

Preferred unsaturated nitriles include acrylonitrile and methacrylonitrile.

The preferred olefinically unsaturated monomers which are free from water-dispersing groups are the alkyl (meth)acrylates containing less than 20 carbon atoms, especially those specifically listed above.

Preferably the water-dissipatable olefinic polymer is an acrylic polymer. An acrylic polymer is preferably a polymer formed from a monomer system comprising at least 40 weight % (more preferably at least 50 weight %) of one or more monomers of formula



where R² is H or methyl and R³ is optionally substituted alkyl of 1 to 12 carbon atoms or cycloalkyl of 5 to 12 (more preferably 1 to 8 and 5 to 8 carbon atoms respectively), examples of which have been given herein.

The water-dissipatable olefinic polymer may be prepared in a conventional manner by polymerising the olefinically unsaturated monomers having water-dispersing groups and olefinically unsaturated monomers having a hydroxy functional group or a group which is convertible to a hydroxy functional group, either alone or in the presence of olefinically unsaturated monomers which are free from water-dispersing and hydroxy functional groups. Temperatures of from 20°C and 180°C are preferred. The polymerisation may be continued until reaction between the monomers is complete.

In one embodiment the olefinic water-dissipatable polymer may be prepared by polymerising an acrylic oligomer having water-dispersing groups and at least one olefinically unsaturated terminal group in the presence of one or more olefinically unsaturated monomers having a hydroxy functional group or a group which is convertible to a hydroxy functional group, and optionally one or more olefinically unsaturated monomers which are free from water-dispersing groups and/or one or more olefinically unsaturated monomers having water-dispersing groups.

Alternatively an acrylic oligomer with at least one olefinically unsaturated terminal group and which is free from water-dispersing groups may be polymerised in the presence of one or more olefinically unsaturated monomers having a hydroxy functional group or a group which is convertible to a hydroxy functional group and one or more olefinically unsaturated monomers having water-dispersing groups.

Preferred polymerisation methods include solution polymerisation, emulsion polymerisation, suspension polymerisation and solution/dispersion polymerisation and such general methods as are well known in the art. More preferably aqueous or non-aqueous solution polymerisation and emulsion polymerisation is used and most preferably solution polymerisation is used.

If desired, an initiator may be used to assist the water-dissipatable olefinic polymer formation. Suitable initiators are free-radical generators. Examples of catalysts include azobis compounds, peroxides, hydroperoxides, redox catalysts, etc., for example, potassium persulfate, ammonium persulfate, tert-butyl peroctoate, benzoyl peroxide, isopropyl percarbonate, 2,4-dichlorobenzoyl peroxide, methyl ethyl ketone peroxide, cumene hydroperoxide, dicumyl peroxide, azobisisobutyronitrile, azobis(2-amidino-propane)hydrochloride and the like.

Typically 0.05 to 5% by weight of initiator is used relative to the total weight of the monomers. Preferably the polymerisation is performed in the presence of an emulsifying agent.

The molecular weight of the olefinic water-dissipatable polymer may be controlled by the addition of chain transfer agents and/or through the adjustment of the ratio of the concentration of monomers relative to the concentration of initiator during the course of the polymerisation. Typical chain transfer agents are thiols, halocarbons and cobalt macrocycles.

When the water-dissipatable polymer is a polyester or polyurethane it may be prepared by conventional techniques, for example as described in PCT/GB99/00656 (polyurethanes) or PCT/GB98/01583 (polyesters) using a monomer carrying a protected hydroxy functional group to form the water-dissipatable polymer followed by removal of the protecting group prior to reaction with a colorant, a colorant precursor, or a bridging compound to give a covalent -O-link.

When the water-dissipatable polymer is prepared by the polymerisation of

(a) monomers having hydroxy functional groups or a group which is convertible to a hydroxy functional group, and (b) monomers providing water-dispersing groups optionally in the presence of (c) monomers which are free from water-dispersing groups and hydroxy functional groups, it is preferred that the amount of (a) is from 1 to 95%, more preferably from 2 to 90% and the amount of (b) is from 1 to 95%, more preferably from 5 to 90% and the amount of (c) is from 0 to 95%, more preferably from 5 to 90% by weight, wherein (a) + (b) + (c) add up to 100.

The water-dissipatable polymer preferably has an acid value of from 0 to 750mgKOH/g, more preferably 50 to 450mgKOH/g, especially 50 to 225mgKOH/g.

Suitable colorants include reactive dyes. Reactive dyes are known in the art as dyes as having functional groups reactive towards hydroxy functional groups. These reactive dyes include, but are not limited to: i) chlorine or fluorine containing reactive dyes, for example dichloro and monochloro triazine reactive dyes, ii) vinyl sulphone or protected vinyl sulphone reactive dyes for example sulphato ethyl sulphone reactive dyes, iii) aziridine functionalised dyes, iv) epoxide functionalised dyes, v) isocyanate functionalised dyes and vi) phosphoric acid functionalised dyes which give ester links on dehydration.

The colorant preferably has at least one functional group capable of reacting with a hydroxy functional group on the water-dissipatable polymer. If two or more such functional groups are present in the colorant, one preferably has a higher reactivity than the other(s) to prevent undesirable cross-linking which results in a non-desirable viscosity increase, making the water-dissipatable polymer less suitable for thermal ink-jet printing inks. Examples of suitable functional groups include alkyl halides, acid chlorides or bromides, reactive aryl and heterocyclic halides, esters, acids (if a catalyst and/or a dehydrating agent is used), reactive olefins and masked reactive olefins (for example vinyl sulphones or acrylates), isocyanates, isothiocyanates, epoxides, aziridines, tosylates, mesylates and other sulphone leaving groups. The functional group may be present in the colorant or grafted to the colorant via a bridging compound.

The colorant preferably has a chromophoric group comprising an azo, anthraquinone, pyrroline, phthalocyanine, polymethine, aryl-carbonium, triphenodioxazine, benzodifuranone or indolene group. Preferred chromophoric groups are azo groups, especially monoazo, disazo, trisazo and phthalocyanine groups.

The colorant may be a single coloured component or a mixture of coloured components, for example it may be a mixture of different dyes. By using a mixture of different dyes as the colorant one may achieve greater flexibility in colour of the ink.

The colorant may also comprise a colorant precursor. For example the colorant precursor may be converted to a colorant by a process comprising a diazotisation reaction. A diazotisation reaction suitably comprises the steps:

(i) diazotising an amino group in the colorant precursor using a diazotising agent; and

(ii) coupling the product of step (i) with a coupling component forming an azo group therebetween.

Preferably the colorant is soluble in organic solvents and/or water, especially water. More preferably the dyes are water soluble anionic or cationic dyes. Most preferably an anionic dye is used to graft onto an anionic water-dissipatable polymer and a cationic dye is used to graft onto a cationic water-dissipatable polymer. Water solubility of the dye may be achieved by the presence of acidic or basic groups in the dye. Preferred acidic groups are phosphonic, carboxylic or sulphonic acids, and combinations and salts thereof.

In a second aspect of the present invention there is provided an ink comprising the components:

(a) a water-dissipatable polymer according to the first aspect of the present invention; and (b) a liquid medium.

Preferably the ink comprises from 0.5 to 50 parts of component (a) and from 50 to 99.5 parts of component (b), wherein all parts are by weight and the number of parts of (a) + (b) = 100. The number of parts of component (a) is preferably from 0.5 to 28, more preferably from 2 to 25, and especially from 2.5 to 20 parts. Preferably component (b) comprises water and an organic solvent. More preferably component (b) comprises from 40 to 95 parts, more preferably from 50 to 90 parts of water; and from 2 to 60 parts, more preferably from 3 to 50 parts, especially from 5 to 35 parts of water-miscible organic solvent. Preferably component (a) is completely dissipated in component (b).

The number of parts of component (a) (the water-dissipatable polymer of the invention) is calculated on a 100% solids basis. For example 50g of a water-dissipatable polymer of the invention in a 20% solids w/w dispersion is taken as 10g of component (a).

The inks according to the second aspect of the invention may be prepared by mixing the water-dissipatable polymer of the invention with a liquid medium. Suitable techniques are well known in the art, for example agitation, ultrasonication or stirring of the mixture. The mixture of water-dissipatable polymer of the invention and liquid medium may be in the form of a dispersion, emulsification, suspension, solution or mixture thereof.

The liquid medium is preferably water, a mixture of water and an organic solvent and an organic solvent free from water. For example the water-dissipatable polymer of the invention may be added to water followed by the addition of one or more organic solvents. Preferably the water-dissipatable polymer of the invention is mixed with a liquid medium, comprising a mixture of water and one or more organic solvents.

When the liquid medium comprises a mixture of water and an organic solvent, the weight ratio of water to organic solvent is preferably from 99:1 to 1:99, more preferably from 99:1 to 50:50, especially from 95:5 to 80:20 and most preferably 90:10.

It is preferred that the organic solvent present in the mixture of water and organic solvent is a water-miscible organic solvent or a mixture of such solvents.

Suitable water-miscible organic solvents include C₁₋₅-alkanols, e.g. methanol, ethanol, n-propanol, isopropanol, n-butanol, sec-butanol, tert-butanol and isobutanol; amides, e.g. dimethylformamide and dimethylacetamide; ketones and ketone alcohols, e.g. acetone and diacetone alcohol; C₂₋₄-ether, e.g. tetrahydrofuran and dioxane; alkylene glycols or thioglycols containing a C₂-C₆ alkylene group, e.g. ethylene glycol, propylene glycol, butylene glycol, pentylene glycol and hexylene glycol; poly(alkylene-glycol)s and thioglycol)s, e.g. diethylene glycol, thiodiglycol, polyethylene glycol and polypropylene glycol; polyols, e.g. glycerol and 1,2,6-hexanetriol; and lower alkyl glycol and polyglycol ethers, e.g. 2-methoxyethanol, 2-(2-methoxyethoxy)ethanol, 2-(2-ethoxyethoxy) ethanol, 2-(2-butoxyethoxy)ethanol, 3-butoxypropan-1-ol, 2-[2-(2-methoxyethoxy)-ethoxy]ethanol, 2-[2-(2-ethoxyethoxy)ethoxy]-ethanol; cyclic esters and cyclic amides, e.g. optionally substituted pyrrolidones; sulpholane; and mixtures containing two or more of the aforementioned water-miscible organic solvents. Preferred water-miscible organic solvents are C₁₋₆-alkyl mono ethers of C₂₋₆-alkylene glycols and C₁₋₆-alkyl mono ethers of poly(C₂₋₆-alkylene glycols).

Suitable water-immiscible organic solvents include aromatic hydrocarbons, e.g. toluene, xylene, naphthalene, tetrahydronaphthalene and methyl naphthalene; chlorinated aromatic hydrocarbons, e.g. chlorobenzene, fluorobenzene, chloronaphthalene and bromonaphthalene; esters, e.g. butyl acetate, ethyl acetate, methyl benzoate, ethyl benzoate, benzyl benzoate, butyl benzoate, phenylethyl acetate, butyl lactate, benzyl lactate, diethyleneglycol dipropionate, dimethyl phthalate, diethyl phthalate, dibutyl phthalate, di (2-ethylhexyl) phthalate; alcohols having six or more carbon atoms, e.g. hexanol, octanol, benzyl alcohol, phenyl ethanol, phenoxy ethanol, phenoxy propanol and phenoxy butanol; ethers having at least 5 carbon atoms, preferably C₅₋₁₄ ethers, e.g. anisole and phenetole; nitrocellulose, cellulose ether, cellulose acetate; low odour petroleum distillates; turpentine; white spirits; naphtha; isopropylbiphenyl; terpene; vegetable oil; mineral oil; essential oil; and natural oil; and mixtures of any two or more thereof. Benzyl alcohol is especially preferred.

The ink optionally contains a biocide, for example Proxel GXL (Proxel is a trade mark of Avecia Limited) or Kathon (Kathon is a trade mark of Rohm and Haas), a fungicide, a rheological agent, e.g. a wax (e.g. beeswax), a clay (e.g. bentonite), an IR absorber, for example Projet 900NP (Projet is a trade mark of Avecia Limited), or a fluorescent brightener, for example C.I.Fluorescent Brightener 179 and/or UV absorber, for example hydroxy phenylbenzotriazole. Furthermore the ink optionally contains a surface active agent, wetting agent and/or an emulsifier, for example those described in McCutcheon's Emulsifiers and Detergents 1996 International Edition or in Surfactants Europa 3rd Edition 1996 each of which is incorporated herein by reference. In a preferred embodiment the ink of the present invention does not contain any pigments.

The ink preferably has a pH from 3 to 11, more preferably from 4 to 10. The pH selected will depend to some extent on the desired cation for colorant and the materials used to construct the ink jet printer head. The desired pH may be obtained by the addition of an acid, base or a pH buffer. Where a base is used this is preferably the same base as was used to neutralise any anionic dispersing group during the preparation of the water-dissipatable polymer of the invention.

5 The viscosity of the ink is preferably less than 20cp, more preferably less than 15cp, especially less than 10cp, at 20°C.

10 Preferably the ink has been filtered through a filter having a mean pore size below 10 µm, preferably below 5 µm, more preferably below 2µm, especially below 0.45 µm. In this way particulate matter is removed which could otherwise block fine nozzles in an ink jet printer.

15 Preferably the ink contains less than 500 ppm, more preferably less than 250 ppm, especially less than 100 ppm of in total of divalent and trivalent metal ions.

20 The inks of the present invention have the advantage that they are suitable not only for the use in piezoelectric ink jet printers but also in thermal and continuous ink jet printers. Many other inks based on polymers work poorly or even not at all in thermal ink jet printers.

25 Inks of the present invention form discrete droplets on the substrate with little tendency for diffusing. Consequently sharp images with excellent print quality and little if any bleed between colours printed side by side can be obtained. Furthermore the inks show good storage stability, wet and light fastness and fastness to both acidic and alkaline highlighter pens.

30 A third aspect of the invention provides a process for printing an image on a substrate comprising applying thereto an ink according to the second aspect of the present invention by means of an ink jet printer.

35 The ink jet printer preferably applies the ink to the substrate in the form of droplets which are ejected through a small nozzle onto the substrate. Preferred ink jet printers are piezoelectric ink jet printers and thermal ink jet printers. In thermal ink jet printers, programmed pulses of heat are applied to the ink in a reservoir by means of a resistor adjacent to the nozzle, thereby causing the ink to be ejected in the form of small droplets directed towards the substrate during relative movement between the substrate and the nozzle. In piezoelectric ink jet printers the oscillation of a small crystal causes ejection of the ink from the nozzle.

40 The substrate is preferably a paper, plastic, or textile material, more preferably a paper, an overhead projector slide or a textile material, especially paper.

Preferred papers are plain, coated or treated papers which may have an acid, alkaline or neutral character. Most preferably the substrate is a coated paper.

According to a fourth feature of the invention there is provided an ink jet printer cartridge, optionally refillable, containing an ink as hereinbefore defined.

The invention will now be described by example only. All parts and percentages are by weight unless specified otherwise. In the examples, compounds referred to by reference to CI numbers are the dyestuffs identified by these numbers in the Colour Index International, 3rd Edition, 3rd Revision.

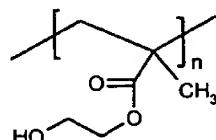
5 Abbreviations used herein:

- MAA = methyl acrylic acid
- MAA = methyl methacrylate
- HEMA = hydroxy ethyl methacrylate
- EHA = ethyl hexylacrylate
- Sty = styrene
- EA = ethyl acrylate
- AIBN = azo-iso-butylnitrile
- β -CEA = β -carboxylate ethyl acrylate
- HPA = hydroxy propylacrylate
- AA = acrylic acid

10 Preparation of Water-dissipatable Polymer 1 carrying hydroxy functional groups

MAA/MMA/HEMA/EHA/EA = 15/34/10/10/31

using components as listed in Table 1 below and where Formula 1 represents a repeat unit of 2-hydroxyethylmethacrylate (HEMA) where n = 10% w/w of the water-dissipatable polymer.



Formula 1

Table 1

25

Component Number	Component	Weight (g)
1	Azo-Iso-Butylnitrile (AIBN)	0.6
2	Butyl-3-Mercaptopropionate	7.0
3	Methyl Ethyl ketone	333.5
4	Methyl Acrylic Acid (MAA)	35.0
5	Methyl Methacrylate (MMA)	79.6
6	Hydroxy Ethyl Methacrylate (HEMA)	23.3
7	Ethyl Hexyl Acrylate (EHA)	23.3
8	Ethyl Acrylate (EA)	71.9
9	Azo-Iso-Butylnitrile (AIBN)	1.7
10	Methyl Ethyl ketone	30.0

5 The initial charge (components 1,2,3,4,5,6,7 and 8) were added to a stirred reaction vessel under a nitrogen atmosphere and heated to 80°C. The initiator feed (components 9 and 10) was charged to a 50 ml syringe. At 80°C, the initiator feed was
10 added slowly to the initial charge mixture via the use of a syringe pump such that the total addition time was three hours. When the addition of the initiator feed was completed, the reaction mixture was left to stir for one hour at 90°C. A monomer 'burn-up' was then carried out by adding V65 initiator 0.2% on solids (V65 = 2,2-azobis(2,4-dimethylvaleronitrile CAS 4419-11-8, V65 is a trade name of Wako) and leaving for a further 40 minutes at 90°C. The product was then cooled to room temperature before being bottled.

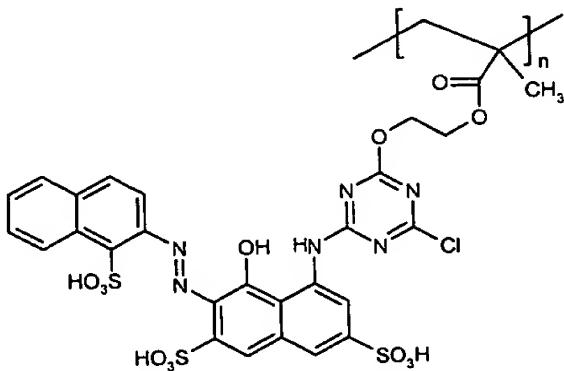
15 The solution of the Water-dissipatable Polymer 1 was found to have a solids content of 40.0%. Molecular weight distribution was done on the Water-dissipatable Polymer 1 by gel permeation chromatography giving Mw = 10550 and Mn = 4760. Purification of the Water-dissipatable Polymer 1 was carried out to remove any unreacted monomer. 10 parts of the water-dissipatable polymer was dissolved in 100 parts of aqueous ammonia (pH 9), cascade filtered and reverse osmosis was carried out until a low conductivity (<100 μ s) was achieved.

20 Example 1: Preparation of Coloured Water-dissipatable Polymer 1:

25 A suspension of the Water-Dissipatable Polymer 1 (9 parts) in water (50 parts) at room temperature was adjusted to pH 9.5 by addition of 2N sodium hydroxide solution. The mixture was stirred for 2 hours and then a solution of CI Reactive Red 11 (30 parts) in water (200 parts) was added dropwise over 10 minutes whilst maintaining pH 9.5 by dropwise addition of 2N sodium hydroxide. The solution was left to stir at pH 9.5 and room temperature for 60 hours and then adjusted to pH 1 by addition of excess 2N hydrochloric acid. The resulting solid was isolated by filtration and washed with copious distilled water. The solid was dissolved in aqueous ammonia, precipitated by acidification to pH 1 with 2N hydrochloric acid, isolated by filtration and washed with distilled water. The dissolving, isolation and precipitation process was then repeated twice.

30 The resultant coloured water-dissipatable polymer was dissolved in aqueous ammonia and the solution was filtered through a cascade of filters (Glass microfibre GF/A, GF/F and membrane) to 0.45 micron and then purified by reverse osmosis using a 3000 MW cut off membrane and evaporated to dryness at approximately 80°C to give Coloured Water-dissipatable Polymer 1 containing a repeat unit of Formula 2:

Formula 2

Preparation of Ink

Inks were prepared by dissolving 10% of the Coloured Water-dissipatable Polymer 1 in a stock solution of 9 parts water and 1 part 1-methyl-2-pyrrolidinone with the addition of concentrated ammonia to give a pH of 9-10. The inks were then filtered through a 0.45 micron membrane filter and printed using an HP 560 thermal IJ printer. The following results (Table 2) were obtained on Gilbert Bond paper:

10

Table 2

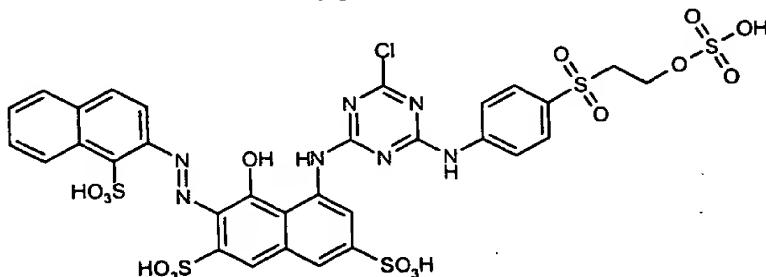
Example 1 % solid in ink	OD Optical Density	a	b	Run down (5 min)
10	0.362	+33.01	-16.92	10
10	0.720	+54.63	-19.47	9

The resultant prints had excellent fastness to acidic and alkaline highlighter pens.

15

Preparation of a colorant of Formula 3 comprising a dye and a bridging compound

Formula 3



20

para-Aminobenzenesulfatoethylsulfone (8 parts) was added to a stirred solution of Cl Reactive Red 11 (20 parts) in water (80 parts) at room temperature and the resulting solution was adjusted to pH 7.0 by addition of 2N sodium hydroxide. The

solution was allowed to stir at pH 7.0 and room temperature overnight and then salt was added until a solid precipitated. The resulting suspension was filtered and the collected coloured paste was washed with brine.

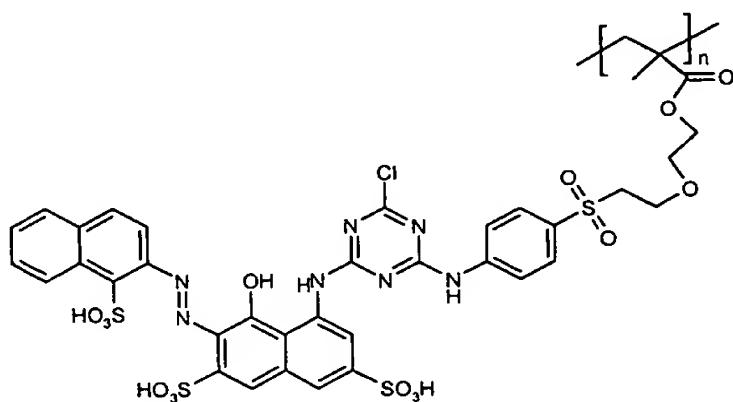
The coloured paste was dissolved in distilled water and the solution was filtered through a cascade of filters (Glass microfibre GF/A, GF/F and membrane) to 0.45 micron and then purified by reverse osmosis using a 500 MW cut off membrane and evaporated to dryness on a rotary evaporator at 40°C to leave the colorant of Formula 3 (13 parts)

10 Example 2: Preparation of Coloured Water-dissipatable Polymer 2:

A suspension of the Water-dissipatable Polymer 1 in water (5 parts) at room temperature was adjusted to pH 12 by addition of 2N sodium hydroxide solution. The mixture was stirred for 2 hours and the colorant of Formula 3, as prepared above (1 part) was added and the solution was readjusted to pH 12. The resulting solution was stirred at pH 12 and room temperature for 72 hours and then adjusted to pH 1 by addition of excess 2N hydrochloric acid. The resulting solid was isolated by filtration and washed with copious distilled water. The solid was dissolved in aqueous ammonia, precipitated by acidification with 2N hydrochloric acid, isolated by filtration and washed with distilled water. The dissolving, isolation and precipitation process was then repeated again.

The resultant coloured water-dissipatable polymer was dissolved in aqueous ammonia and the solution was filtered through a cascade of filters (Glass microfibre GF/A, GF/F and membrane) to 0.45 micron and then purified by reverse osmosis using a 3000 MW cut off membrane and evaporated to dryness at approximately 80°C to give the Coloured Water-dissipatable Polymer 2 containing a repeat unit of Formula 4:

Formula 4



Preparation of Ink

An ink was prepared by dissolving 10% of the Coloured Water-dissipatable Polymer 2 in a stock solution of 9 parts water and 1 part 1-methyl-2-pyrrolidinone with the addition of concentrated ammonia to give a pH of 9-10. The ink was then filtered through a 0.45 micron membrane filter and printed using an HP 560 thermal Ink-Jet printer. The following results (Table 3) were obtained on Gilbert Bond paper

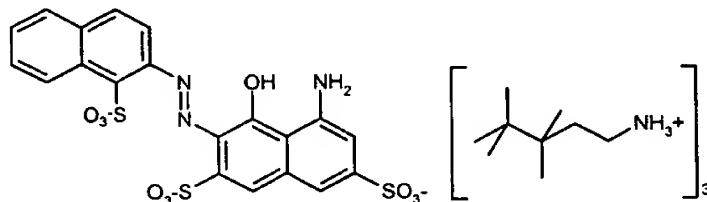
Table 3

Example 2 % Solid in Ink	OD	a	b	Run Down (5 min)
10	0.738	+31.07	-17.66	10

The resultant print had excellent fastness to acidic and alkaline highlighter pens. The print lost 5% OD on fading for 100 hours in an accelerated light fastness test.

Preparation of a iso-nonylamine salt of a colorant of Formula 5

Formula 5



iso-Nonylamine (6 parts) was dissolved in distilled water (150 parts) and set stirring. A solution of a dye base of Cl Reactive Red 11 sodium salt (5 parts) in water (50 parts) was screened through a GF/F filter and added dropwise over 30 minutes to the solution of iso-nonylamine, maintaining pH 7.0 by addition of 2N hydrochloric acid. The mixture was stirred for 30 minutes and then the resulting suspension was filtered to give a paste. The collected paste was washed with water (20 parts) and then dried at room temperature and under reduced pressure over phosphorus pentoxide for 24 hours to leave a red solid colorant of Formula 5.

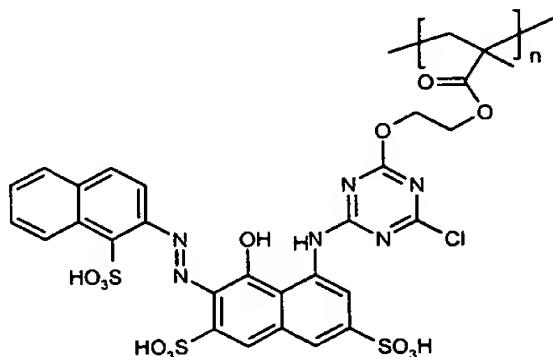
Example 3: Preparation of Coloured Water-dissipatable Polymer 3:

Cyanuric chloride (1.3 parts) and potassium carbonate (1 part) were added to a stirred solution of Water-dissipatable Polymer 1 (10 parts) in tetrahydrofuran (110 parts) at room temperature. The resulting mixture was stirred for 2 hours and then a solution of the colorant of Formula 5 (130 parts), triethylamine (1.1 parts) and

N,N-dimethylaminopyridine (0.2 parts) in dimethylformamide (260 parts) was added in one portion. The solution was left to stir for 60 hours and then pored onto vigorously stirred water (3000 parts). The resulting precipitate was collected by filtration and washed with copious distilled water. The solid was dissolved in aqueous ammonia, precipitated by acidification with 2N hydrochloric acid, isolated by filtration and washed with distilled water. The dissolving, isolation and precipitation process was then repeated again.

The resultant coloured water-dissipatable polymer was dissolved in aqueous ammonia and the solution was filtered through a cascade of filters (Glass microfibre GF/A, GF/F and membrane) to 0.45 micron and then purified by reverse osmosis using a 3000 MW cut off membrane and evaporated to dryness at approximately 80°C to give a Coloured Water-dissipatable Polymer 3 containing a repeat unit of Formula 6:

Formula 6



15

Preparation of Ink

An ink was prepared by dissolving 10% of the Coloured Water-dissipatable Polymer 3 in a stock solution of 9 parts water and 1 part 1-methyl-2-pyrrolidinone with the addition of concentrated ammonia to give a pH of 9-10. The ink was filtered through a 0.45 micron membrane filter and printed using an HP 560 thermal Ink-Jet printer. The following results (Table 4) were obtained on Gilbert Bond paper:

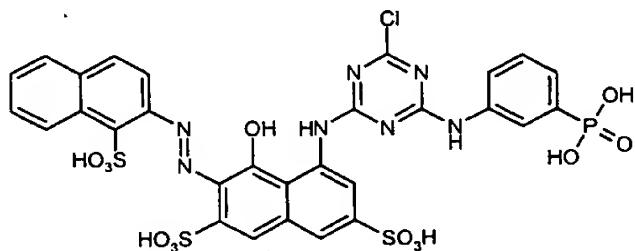
Table 4

25

Example 3 % Solid in Ink	OD	a	b	Run Down (5 min)
10	0.393	+30.37	-13.69	10

Preparation of a phosphonic acid colorant of Formula 7

Formula 7



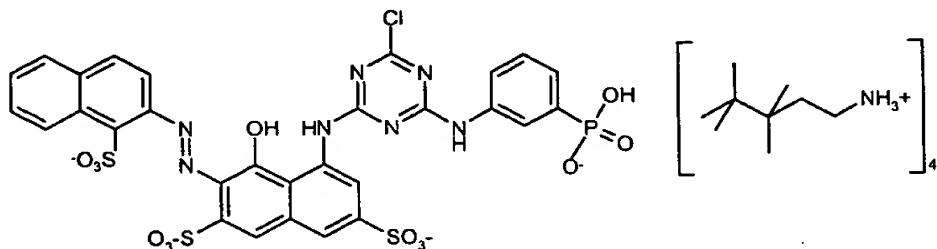
5

Meta-Aminophenylphosphonic acid (5 parts) was added to a stirred solution of Cl Reactive Red 11 (20 parts) in water (80 parts) at room temperature and the resulting solution was adjusted to pH 7.0 by addition of 2N sodium hydroxide. The solution was allowed to stir at pH 7.0 and room temperature overnight and then salt was added until a solid precipitated. The resulting suspension was filtered to give a coloured paste and the paste was washed with brine.

The coloured paste was dissolved in distilled water and the resultant solution was filtered through a cascade of filters (Glass microfibre GF/A, GF/F and membrane) to 0.45 micron and then purified by reverse osmosis using a 500 MW cut off membrane and evaporated to dryness on a rotary evaporator at 40°C to leave the colorant of Formula 7 (9 parts)

20 Preparation of a iso-nonylamine salt (Formula 8) of the phosphonic acid colorant of Formula 7

Formula 8



25

iso-Nonylamine (8 parts) was dissolved in distilled water (150 parts) and set stirring. A solution of the phosphonic acid colorant of Formula 7 as prepared above (9 parts) in water (70 parts) was screened through GF/F filter and added dropwise over 30 minutes to the solution of iso-nonylamine, maintaining pH 7.0 by addition of 2N hydrochloric acid. The mixture was stirred for 30 minutes and then the resulting

30

suspension was filtered. The collected paste was washed with water (20 parts) and then dried at room temperature and under reduced pressure over phosphorus pentaoxide to leave a red solid (10 parts) colorant of Formula 8.

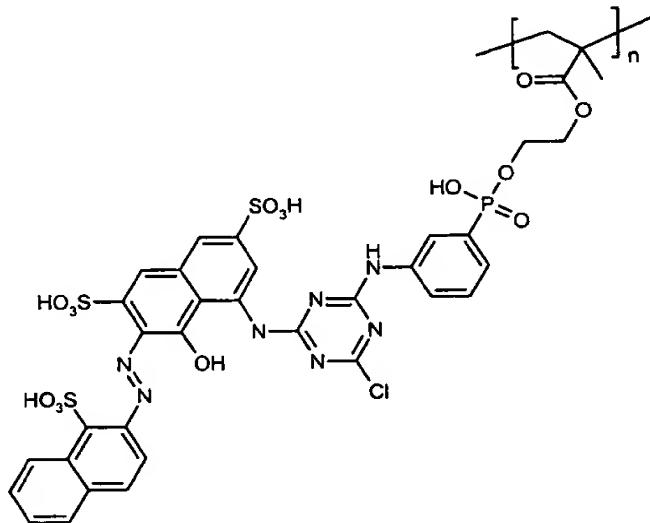
5 Example 4: Preparation of a Coloured Water-dissipatable Polymer 4

The Water-dissipatable Polymer 1 (2 parts), dicyandiamide (1.3 parts) and the colorant of Formula 8 (3 parts) were added to dimethylformamide (30 parts) and set stirring. The solution was heated to 130°C for 72 hours and then cooled to room temperature and poured onto water (300 parts). The resultant suspension was adjusted to pH 10 with aqueous ammonia and then the resulting solution was adjusted to pH 1 by addition of 2N hydrochloric acid. The supernatant liquid was decanted and the resulting tar-like material was dissolved in acetone (30 parts) and diluted with water (300 parts).

10 The resultant suspension was adjusted to pH 10 with aqueous ammonia and the solution was filtered through a cascade of filters (Glass microfibre GF/A, GF/F and membrane) to 0.45 micron and then purified by reverse osmosis using a 3000 MW cut off membrane and evaporated to dryness at approximately 80°C to give a Coloured Water-dissipatable Polymer 4 containing a repeat unit of Formula 9:

Formula 9

20

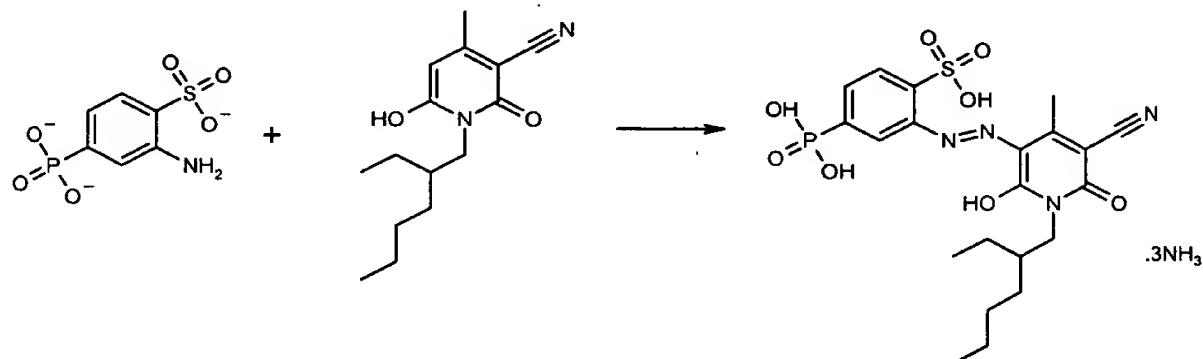


Preparation of ink

An ink was prepared by dissolving the 10% of the Coloured Water-dissipatable Polymer 4 in a stock solution of 9 parts water and 1 part 1-methyl-2-pyrrolidinone with the addition of concentrated ammonia to give a pH of 9-10. The ink was then filtered through a 0.45 micron membrane filter and printed using an HP 560 thermal Ink-Jet printer. The following results (Table 5) were obtained on Gilbert Bond paper:

Table 5

Example 4 % Solid in Ink	OD	a	b	Run Down (5 min)
10	0.865	+53.95	-15.91	9

5 Preparation of colorant of Formula 12

10 Formula 10

Formula 11

Colorant of Formula 12 as
ammonia salt

15 The 2-amino-4-phosphonic acid benzene sulphonate (Formula 10) (40 parts) was stirred in water (600 parts) and the mixture was adjusted to pH 5.0 by addition of 48% sodium hydroxide solution. The resulting solution was cooled to 0-10°C and 150 parts concentrated hydrochloric acid were added. To this mixture 75 parts of 2N Sodium nitrite were added and the mixture was allowed to stir for 10 minutes. Any excess nitrous acid was destroyed by the addition of sulphamic acid.

20 The pyridone (Formula 11) (42 parts) was dissolved in water (200 parts) at pH 8 by addition of 48% sodium hydroxide solution. This solution was added to the above mixture and adjusted to pH 5 by addition of sodium acetate. More pyridone (Formula 11) (10 parts) was added and the resulting mixture was allowed to warm to room temperature over night. The resulting mixture was filtered to leave a paste.

25 The paste was dissolved in water (600 parts) and adjusted to pH 9 by addition of ammonia and then added to concentrated hydrochloric acid (60 parts) and stirred for 15 minutes and then filtered to leave a paste. The paste was dissolved in water at pH 9 by addition of ammonia and the solution was dialysed to a conductivity of <100μs then filtered through a cascade of filters, (Glass microfibre, GF/A, GF/F and membrane) to

0.45 micron and dried in the oven at 60°C to give 21 parts of a colorant of Formula 12 as a yellow solid.

Preparation of an iso-nonylamine salt of a colorant of Formula 12

iso-Nonylamine (20 parts) was dissolved in distilled water (700 parts) and set stirring. A solution of the colorant of Formula 10 salt (16 parts) in water (300 parts) was screened through GF/F filter and added dropwise over 30 minutes to the solution of iso-nonylamine, maintaining pH 7.0 by addition of 2N hydrochloric acid. The mixture was stirred for 30 minutes and then the resulting suspension was filtered to give a paste. The collected paste was washed with water (200 parts) and then dried at room temperature and under reduced pressure over phosphorus pentaoxide for 24 hours to give the iso-nonylamine salt of colorant of Formula 12 as a yellow solid.

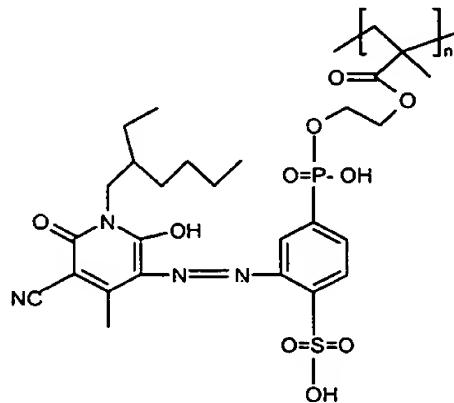
Example 5: Preparation of Coloured Water-dissipatable Polymer 5.

The iso-nonylamine salt of colorant of Formula 12 prepared above (80 parts) and dicyanimide (20 parts) were added to a stirred solution of Water-dissipatable Polymer 1, (100 parts) in dimethylformamide (2000 parts) at room temperature. The resulting mixture was stirred for 7 hours at 100°C then cooled to room temperature and stirred overnight.

Dicyanimide (20 parts) was added and the mixture was stirred at 100°C for 7 hours. The resulting solution was poured into water (5000 parts) and the resulting precipitate was collected by filtration and washed with copious distilled water. The solid acid, was isolated by filtration and washed with distilled water. The dissolving, isolation and precipitation process was then repeated again.

The resultant coloured water-dissipatable polymer was dissolved in aqueous ammonia and the solution was filtered through a cascade of filters (Glass microfibre GF/A, GF/F and membrane) to 0.45 micron and then purified by reverse osmosis using a 3000 MW cut off membrane and evaporated to dryness at approximately 80°C to give a Coloured Water-dissipatable Polymer 5 containing a repeat unit of Formula 13:

Formula 13



Preparation of Ink

An ink was prepared by dissolving the 10% of the Coloured Water-dissipatable Polymer 5 in a stock solution of 9 parts water and 1 part 1-methyl-2-pyrrolidinone with the addition of concentrated ammonia to give a pH of 9-10. The ink was filtered through a 0.45 micron membrane filter and printed using an HP 560 thermal Ink-Jet printer.

The following results (Table 6) were obtained on Gilbert Bond paper:

Table 6

Example 5 % Solid in Ink	OD	a	b	Run Down (5 min)
10	0.504	-15.19	55.90	10

Examples 6 to 9

Example 1 may be repeated except that in place of Water-Dissipatable Polymer 1 there is used the following water-dissipatable polymer:

Example 6 MMA/Sty/MAA/HEMA 30/30/20/20

Example 7 MMA/Sty/AA/DEA 30/10/45/15

Example 8 MMA/MAA/ β CEA/HPA 40/30/10/20

Example 9 MMA/Sty/MAA/HEMA/TONEM100 30/10/40/10/10

Examples 10 to 25

Example 1 may be repeated except that in place of CI Reactive Red 11 there is used CI Reactive Blue 81, CI Reactive Red 2, CI Reactive Yellow 4, CI Reactive Blue 89, CI Reactive Brown 21, CI Reactive Red 63, CI Reactive Yellow 75, CI Reactive Black 5, CI Reactive Red 194, CI Reactive Red 195, CI Reactive Yellow 145, CI Reactive Blue 173, CI Reactive Orange 89, CI Reactive Red 179, or CI Reactive Yellow 133.

Example 26

Further inks may be prepared having the formulations described in Tables 7 and 8 below wherein the following abbreviations are used. The number of parts by weight of each component is given. Water is included in each formulation to make the total number of parts up to 100. These inks may be applied to plain paper using an Ink-Jet printer.

FRU : fructose

CAP 1 to 9 : Identifies which of the coloured water-dissipatable polymers as prepared in Examples 1 to 9 may be used. The number of parts by weight of CAP is shown in the second column

BZ : Benzyl alcohol

DEG : Diethylene glycol

	DMB	: Diethyleneglycol monobutyl ether
	ACE	: Acetone
	IPA	: Isopropyl alcohol
	MEOH	: Methanol
5	2P	: 2-Pyrollidone
	MIBK	: Methylisobutyl ketone
	SUR	: Surfinol 465 (a surfactant)
	PHO	: K ₂ PO ₄
	TEN	: triethanolamine
10	NMP	: N-methylpyrrolidone
	TDG	: Thiodiglycol
	CAP	: Caprolactam
	BUT	: Butylcellosolve
	GLY	: Glycerol

TABLE 7

CAP*	CAP (parts by weight)	BZ	DEG	ACE	NaOH	$(\text{NH}_4)_2\text{SO}_4$	IPA	MEOH	2P	MIBK	BUT
1	6	4	6		0.2				10	15	
2	3	5	5						20	1	3
3	10	8			0.5	0.5			8	4	1
4	4	8							5	4	
1+2	(4+4)	15	3	3					20	5	1
6	5	20									
2	3	4	5	10		6	6	6	20	5	
5	4	5	2	10							
4	10	6	6	6							
4	5	6	2	2							
2	2	5									
5	4	5									
7	2.0	15									
8	6	20	2	1	0.3				10	15	3
9	1.0	5	4						20	5	

TABLE 8

CAP*	CAP (parts by weight)	BZ	NMP	SUR	TEN	TDG	FRU	PHO	DMB	CH ₃ NH ₂	CAP
4	2	5	0.15	0.4	20			0.05			4
6	3	6	15								2
5	10	10	0.3		15		0.5	0.2			
3	1	10	20								
2	8	15	15	0.2	1	5					
1	5	10	10								
7	3	5	3								
4	10	9	7	0.5		12					
8	5	11									
3	6	5	17								
5	5	8	5	0.1	0.2		2	0.5	0.1		
2	2	10	5				10				
4	8	5	8								
9	10	4									
1	10	10	1				1	1			
									12	9	2
									1	1	1

CLAIMS

1. A water-dissipatable polymer having colorant attached thereto through a covalent -O- link.
5
2. A water-dissipatable polymer according to claim 1 obtainable by the reaction of a water-dissipatable polymer with pendant hydroxy functional groups with a colorant having a functional group capable of reacting with hydroxy functional groups.
- 10 3. A water-dissipatable polymer according to claim 1 wherein the colorant is attached thereto by means of a reaction between a hydroxy group on the polymer with a colorant precursor thereby forming a covalent bond therebetween and subsequently converting the colorant precursor to a colorant
- 15 4. A water-dissipatable polymer according to claim 1 wherein the colorant is attached thereto by means of a reaction between a hydroxy group on the polymer with a bridging compound thereby forming a covalent bond therebetween and subsequently reacting the bridging compound with a colorant or colorant precursor.
- 20 5. A water-dissipatable polymer according to claim 4 wherein the colorant precursor is converted to a colorant by a process comprising a diazotisation reaction.
6. A water-dissipatable polymer according to claim 5 wherein the diazotisation reaction comprises the steps:
25 (i) diazotising an amino group in the colorant precursor using a diazotising agent; and
(ii) coupling the product of step (i) with a coupling component forming an azo group therebetween.
- 30 7. A water-dissipatable polymer according to anyone of the preceding claims wherein the polymer is an olefinic polymer.
8. A water-dissipatable polymer according to claim 7 wherein the olefinic polymer is obtainable from the polymerisation of one or more olefinically unsaturated monomers having water-dispersing groups, and one or more olefinically unsaturated monomers having hydroxy functional groups optionally in the presence of one or more olefinically unsaturated monomers which are free from water-dispersing and hydroxy functional groups.
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9. A water-dissipatable polymer according to any one of the preceding claims wherein the water-dissipatable polymer has a Mn less than 25,000.

10. An ink comprising the components:

- 5 (a) a water-dissipatable polymer according to any one of claims 1 to 9; and
(b) a liquid medium.

11. An ink according to claim 10 wherein component (a) is completely dissipated in component (b).

10

12. An ink according to claim 10 or 11 which comprises from 0.5 to 50 parts of component (a) and from 50 to 99.5 parts of component (b), wherein all parts are by weight and the number of parts of (a) + (b) = 100.

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13. An ink according to claim 10, 11 or 12 wherein component (b) comprises water and an organic solvent.

14. An ink according to claim 13 where component (b) comprises from 40 to 95 parts of water and from 2 to 60 parts of water-miscible organic solvent.

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15. An ink according to any one of claims 10 to 14 having a viscosity less than 20 cp at 20°C.

25

16. An ink according to any one of claims 11 to 15 for use in an ink jet printer.
17. A process for forming an image on a substrate comprising applying thereto an ink using an ink jet printer, characterised in that the ink is as defined in any one of claims 11 to 15.

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18. A paper or an overhead projector slide printed with an ink as defined in any one of claims 11 to 15.

19. An ink jet printer cartridge, optionally refillable, containing an ink as defined in any one of claims 11 to 15.

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INTERNATIONAL SEARCH REPORT

Inter. Application No
PCT/GB 99/04209

A. CLASSIFICATION OF SUBJECT MATTER
 IPC 7 C09D11/00 C09B69/10

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 C09B C09D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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X	FR 1 523 820 A (DAINICHISEIKA COLOR & CHEMICALS) 18 September 1968 (1968-09-18) page 2, column 1, paragraph 4 -page 3, column 1, paragraph 1 page 4, column 1, last paragraph page 12, column 2, last paragraph	1-19
X	EP 0 535 490 A (BASF AG) 7 April 1993 (1993-04-07) claim 1	1-19



Further documents are listed in the continuation of box C.



Patent family members are listed in annex.

* Special categories of cited documents :

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INTERNATIONAL SEARCH REPORT

International Application No
PCT/GB 99/04209

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